

Before the
NATIONAL TOXICOLOGY PROGRAM
BOARD OF SCIENTIFIC COUNSELORS'
REPORT ON CARCINOGENS SUBCOMMITTEE

**COMMENTS IN SUPPORT OF THE PROPOSED DELISTING
OF ETHYL ACRYLATE
FROM THE BIENNIAL REPORT ON CARCINOGENS**

**SUBMITTED BY THE
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COMMENTS OF THE BASIC ACRYLIC MONOMER MANUFACTURERS

The Basic Acrylic Monomer Manufacturers, Inc. ("BAMM") appreciates this opportunity to provide further input to the NTP Board of Scientific Counselors' Report on Carcinogens Subcommittee in support of the proposed delisting of ethyl acrylate from the Biennial Report on Carcinogens ("BRC"). BAMM represents domestic manufacturers of acrylic acid and acrylate esters, including ethyl acrylate.

BAMM filed a delisting petition in August 1997 which led to the current NTP consideration of delisting ethyl acrylate from the BRC. Ethyl acrylate was listed as "reasonably anticipated to be a carcinogen" in 1989 based on a NTP chronic gavage study which induced forestomach tumors in male and female mice and rats. BAMM's petition to delist ethyl acrylate was based on the following data and considerations:

1. A series of subsequent mechanistic studies, most prominently those by NTP scientists, demonstrated that gavage dosing of ethyl acrylate produced localized inflammation and hyperplasia at the site of contact in the rodent forestomach. This response was reversible unless daily gavage dosing continued for six months, in which case the lesions progressed to tumors. The observed response was concentration rather than dose-dependent. No such toxicity or carcinogenicity was observed in the rodent glandular stomach, which received a comparable dose to that of the forestomach.
2. Chronic animal studies employing other routes of exposure, including inhalation, dermal and drinking water exposure, produced no increase in tumors and no toxic response other than slight irritation at the point of contact. Drinking water exposure involving the same daily dose used in the NTP chronic gavage study produced no carcinogenic or toxic response.
3. Extensive metabolic data demonstrates that ethyl acrylate is rapidly metabolized in the body into non-toxic metabolites. Any toxic effects of ethyl acrylate would therefore be expected to occur only at the point of contact. This is confirmed by the lack of any systemic toxicity in any of the numerous studies on ethyl acrylate.

4. While ethyl acrylate produces a positive response in certain types of *in vitro* genotoxicity assays (e.g., mouse lymphoma assay), it generally does not produce a genotoxic response in *in vivo* studies. Recent studies demonstrate that the positive *in vitro* results occur only at concentrations associated with high levels of cytotoxicity.
5. Human ethyl acrylate exposures are almost exclusively via inhalation, with some potential for dermal exposure in occupational settings. Exposures are very low in both occupational and non-occupational settings. The strong, noxious odor of ethyl acrylate at very low concentrations (odor threshold of approx. 0.5 ppb) ensures that human exposure remains negligible. Human exposure levels therefore never approach the very high concentrations of ethyl acrylate needed to overwhelm the detoxification pathways even in the most sensitive rodent forestomach tissue.

These points are elaborated along with the supporting data in the BAMM petition.

BAMM does not seek to repeat the scientific discussion in its petition here, or to provide a comprehensive analysis of the reasons why it believes that ethyl acrylate should be delisted, as that analysis is provided in the BAMM petition. Rather, these comments relate to the Draft Background Document for Ethyl Acrylate ("Background Document") prepared by the NTP. BAMM generally supports the analysis and conclusions in the Background Document, which provides an accurate overview of the key relevant data. These comments provide supplementary studies and analyses to assist the Subcommittee's review of ethyl acrylate.

I. Uses of Ethyl Acrylate

The primary uses of ethyl acrylate are correctly identified in the Background Document as the manufacture of polymers or copolymers used as ingredients in latex paints, industrial coatings, binders, caulks, lubricating oils, polishes, adhesives, acrylic fibers, and plastics. The Background Document also lists a number of other miscellaneous uses of ethyl acrylate, such as use in denture materials, as a fragrance additive or as a synthetic fruit essence. To the knowledge of BAMM and its members, ethyl acrylate has not been used at least in those listed applications for many years, if ever. Nor has BAMM been able to identify the original source of those listed uses, except that they appear to trace back to the 1986 IARC report on ethyl acrylate or earlier.

It is also important to note that all applications of ethyl acrylate in consumer products involve the use of polymerized ethyl acrylate, which contain only trace levels of unreacted residual ethyl acrylate monomer. The various ethyl acrylate polymers used in consumer products are very large molecules (>1 million daltons) that are unlikely to be biologically active.

II. Human Exposure

As the Background Document notes (p. v), ethyl acrylate has a strong acrid odor with a very low odor threshold (~0.5 ppb). Experience indicates that workers and especially consumers will not tolerate ongoing exposures to ethyl acrylate above the odor threshold.

As the Background Document indicates, the recent occupational exposure data collected by BAMM members and others show that worker exposures to ethyl acrylate are consistently well below the 5 ppm threshold limit value ("TLV") and 15 ppm short-term exposure limit ("STEL"). See Background Document at v-vi; see also BAMM Petition at 9-12.

The Background Document does, however, note (p. vi) that "exposure of painters in an unventilated room has been reported as high as 8 ppm in the painter's breathing zone." The data referred to is from a study described in the BAMM Petition (p. 12) and presented in McLaughlin, J.E., Baldwin, R.C. and Smith, J.M. (1993). Ethyl Acrylate Health Effects Assessment, in *Health Effect Assessments of the Basic Acrylates*, (T. Tyler, S. Murphy & E. Hunt, eds.) (CRC Press), pp. 53-81, at 60-61 (BAMM Petition, Exhibit 53). It is important to note that the paint samples used in this study were not commercially available paints, but rather specially formulated samples "spiked" with very high levels of ethyl acrylate. This study used the very high residual monomer levels to establish a "dilution factor" to relate monomer concentration in a wall paint to the concentration of the monomer in the ambient air under different ventilation scenarios. The two paint samples contained 940 and 2000 ppm ethyl acrylate, which resulted in exposure levels of 2.5 and 8.0 ppm, respectively, in an unventilated room. When a ventilated room was used, airborne concentrations of ethyl acrylate were below the detectable level (0.2 ppm).

A BAMM member company has recently conducted a basket survey of latex paints to obtain actual data on ethyl acrylate levels in commercially available paints. The study is attached to these comments at Tab 1. In a sample of 13 brands of flat latex wall paint, residual ethyl acrylate levels averaged 1.28 ppm, with a standard deviation of 1.13 ppm (Tab 1 at 19). In 17 samples of indoor trim paint, ethyl acrylate averaged 4.06 ppm, with a standard deviation of 3.66 ppm (Tab 1 at 20.) These levels of ethyl acrylate residuals in latex paint are therefore 2-3 orders of magnitude lower than the concentrations used in the simulated exposure study discussed in the previous paragraph.

Using the "dilution factors" calculated in the simulated exposure study, ethyl acrylate in latex paint would produce a maximum indoor air concentration, in completely unventilated conditions, of approximately 4 ppb. (Tab 1 at 21.) Of course, adequate room ventilation, which is recommended on the paint can label, would result in much lower airborne concentrations. Nevertheless, even the 4 ppb ambient maximum air levels in an unventilated room is over 1000-fold

lower than the 5 ppm no-observed-adverse-effect-level (NOAEL) for nasal irritation observed in the chronic inhalation study with ethyl acrylate.¹

This recent study of residual ethyl acrylate levels in latex paint is consistent with the findings of EPA's recent analysis in "RM1 Dossier: Wall Paints Indoor Air Screening Cluster, Final Draft Report" (May 30, 1997), which is attached as Appendix A to Tab 1 of these comments. The EPA study analyzed chemical exposures from various types of paint, and was unable to detect any ambient ethyl acrylate from the use of non-solvent latex paints, the only type of paints in which ethyl acrylate is used.

III. Human Studies

The only published epidemiology study involving ethyl acrylate was the cohort study of Walker *et al.* that evaluated three cohorts of workers in two plants producing and using acrylate monomers including methyl methacrylate and ethyl acrylate.² An increase in colon and rectum cancer was observed in one of the cohorts consisting of workers employed before or during World War II. No such increase was observed in the other two cohorts. As the Background Document correctly notes, this study did not distinguish between exposure to ethyl acrylate and methyl methacrylate monomers, could not evaluate the possible confounding effect of the many carcinogenic substances known to be present in that worksite, did not have quantitative exposure data available, and involved a relatively small number of cases. See Background Document at 9. BAMM therefore agrees with the conclusion of the Background Document that this study "can neither establish nor rule out a causal relationship of ethyl acrylate with cancer." (p. vi). See also BAMM Petition at 17-20.

BAMM commissioned the principal author of the cohort study, Dr. Alexander Walker, Chair of the Harvard Department of Epidemiology, to provide his views of the study and its implications for the NTP listing of ethyl acrylate. Dr. Walker's analysis is attached at Tab 2, and it generally supports the position summarized in the NTP Background Document. In addition to agreeing with the points in the Background Document, Dr. Walker notes one other reason why his cohort study cannot be used to either establish or rule out a causal relationship between ethyl acrylate and cancer. As his attached letter explains, the study was "a *post hoc* analysis of an unexpected finding" that was initially observed in a company study designed and undertaken to evaluate respiratory cancer. The observed increase in colon and rectal cancer in one of the three cohorts that was evaluated was therefore not an *a priori* hypothesis. An increase in a single type of cancer, of a type not expected given the exposure routes and information on the rapid metabolism of the chemical,

¹ Miller, R.R., Young, J.T., Kociba, R.J., Keyes, D.G., Bodner, K.M., Calhoun, L.L. and Ayres, J.A. (1985). Chronic toxicity and oncogenicity bioassay of inhaled ethyl acrylate in Fischer 344 rats and B6C3F1 mice. *Drug Chem. Toxicol.* 8:1-42 (BAMM Petition, Exhibit 54).

² Walker, A. M., Cohen, A. J., Loughlin, M. S., Rothman, K. J. and DeFonso, L. R. (1991). Mortality from cancer of the colon or rectum among workers exposed to ethyl acrylate and methyl methacrylate. *Scand. J. Work Environ. Health* 17:7-19 (BAMM Petition, Exhibit 90).

in a single cohort and study is generally not considered to establish a causal relationship in epidemiology, especially given the many confounding exposures in that particular workplace before and during World War II.

A final point on the Walker *et al.* study is that EPA reviewed the study earlier this year in preparing an IRIS "Toxicological Review" for methyl methacrylate,³ likely the chemical involving the highest exposure in the Walker *et al.* study. After noting the various shortcomings of the study for evaluating a causal association between the exposures in the plant and the increased colon-rectal cancer mortality in the one subcohort, EPA concluded that the "human epidemiologic evidence is inadequate for basing a carcinogenicity determination," and classified methyl methacrylate as "not likely to be carcinogenic to humans." The relevant pages from the EPA document are attached at Tab 3.

IV. Experimental Carcinogenesis

The Background Document summarizes the results of chronic animal studies of ethyl acrylate involving four different routes of exposure: (i) inhalation; (ii) gavage; (iii) drinking water; and (iv) dermal. Background Document at 12-14; *see also* BAMM Petition at 13-16. As the Background Document notes, the only increase in tumors observed in any of the studies was in the forestomach after gavage dosing.

In addition to the studies described in the Background Document, chronic inhalation studies have been completed for the closely related compounds butyl acrylate and methyl acrylate, which provides additional support that ethyl acrylate is not carcinogenic via inhalation. Butyl acrylate and methyl acrylate have structures very similar to ethyl acrylate, and like ethyl acrylate are rapidly hydrolyzed by esterases in tissues to release acrylic acid. The chronic studies of butyl acrylate and methyl acrylate observed the same nasal irritation effects as were observed in the ethyl acrylate chronic inhalation study, but like the ethyl acrylate study, found no increase in tumors or indications of systemic toxicity.⁴ A subchronic inhalation study of the parent compound acrylic acid likewise observed the same nasal irritation effects, but no other indications of toxicity or carcinogenicity.⁵

³ EPA, Toxicological Review of Methyl Methacrylate, In Support of Summary Information on the Integrated Risk Information System (IRIS) (Jan. 1998) (Tab 3).

⁴ Reininghaus, W., Koestner, A. and Klimisch, H.-K. (1991). Chronic toxicity and oncogenicity bioassay of inhaled methyl acrylate and n-butyl acrylate in Sprague-Dawley rats. *Food Chem. Toxicol.* 29:329-339 (BAMM Petition, Exhibit 74).

⁵ Miller, R.R., Ayres, J.A., Jersey, G.C. and McKenna, M.J. (1981). Inhalation toxicity of acrylic acid. *Fund. Appl. Toxicol.* 1:271-277 (BAMM Petition, Exhibit 55).

V. Genotoxicity

The Background Document summarizes the extensive available data on the genotoxicity of ethyl acrylate (pp. 15-17), which can be summarized as positive results (chromosome aberrations) in some *in vitro* assays but generally negative results in *in vivo* assays. See also BAMM Petition at 20-25.

An additional study on ethyl acrylate genotoxicity by Ciaccio *et al.* has recently been accepted for publication in the journal *Toxicological Sciences*, and a copy of the accepted manuscript is attached at Tab 4. The study evaluated the relationship between ethyl acrylate-induced cytotoxicity and the mutations observed in the mouse lymphoma assay. The study found that ethyl acrylate did not induce single-strand DNA breaks in the alkaline elution assay, and therefore did not appear to be directly genotoxic. The study observed double-strand DNA breaks only at the highest concentrations, which appeared to be associated with extensive cytotoxicity mediated by nonprotein sulfhydryl depletion and mitochondrial membrane impairment. These results suggest that the genotoxic response observed in some *in vitro* assays at high concentrations of ethyl acrylate may be associated with cytotoxicity that indirectly results in DNA breaks and genotoxicity. These effects are not observed in the *in vivo* assays likely because ethyl acrylate is so rapidly metabolized in tissues that the high concentrations needed to induce cytotoxicity are not achieved. This analysis is consistent with another recently published study by Hilliard *et al.* (Tab 5) which found that nonmutagenic noncarcinogens at toxic levels can induce chromosome aberrations by secondary mechanisms associated with cytotoxicity.

The Background Document notes that ethyl acrylate did not produce tumors after dermal application to female mice of the transgenic Tg.AC line, but stated that the experimental details were not presented in the Tennant *et al.* (1996) paper that first summarized those experimental results. (Background Document, p. 17). The full experimental details of that study have now been published by Nylander-French and French (1998), which is attached at Tab 6.

VI. Other Data Relevant to an Evaluation of Carcinogenicity and Its Mechanisms

The Background Document summarizes the elegant series of studies by NTP scientists that investigated the mechanism by which ethyl acrylate produced forestomach tumors in the mice and rat after chronic gavage dosing. (Background Document at 18-19). These experiments are central to the BAMM delisting petition, as they demonstrate that the only tumors observed in the chronic animal studies of ethyl acrylate are associated with chronic inflammation and hyperplasia that only develops into tumors in the presence of continued long-term exposure to high concentrations of ethyl acrylate, which is highly unlikely to occur in humans. Additional studies by other laboratories, which are attached to the BAMM Petition, have further confirmed and supported the original findings of the NTP scientists. See BAMM Petition at 33-46.

Conclusion

Compelling high-quality data now exist that ethyl acrylate does not present a human carcinogenic hazard. BAMM therefore respectfully urges the Subcommittee to support the NTP recommendation to delist ethyl acrylate from the Biennial Report on Carcinogens.

RM1 Dossier:

*WALL PAINTS
INDOOR AIR SCREENING CLUSTER*

Final Draft Report

May 30, 1997

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1.0 OVERVIEW AND SELECTION RATIONALE

The evaluation of wall paints as a source of indoor air pollution began under the Indoor Air Source Characterization Project (IASCP). The IASCP is a multi-year, intra-agency project within the U.S. Environmental Protection Agency (EPA), jointly led by the Office of Radiation and Indoor Air (ORIA), the Office of Pollution Prevention and Toxics (OPPT), and the Office of Research and Development (ORD). The purpose of the project is to determine those classes of products that are major contributors to indoor air exposures and risks, and to take actions, as necessary, to reduce exposures and risks.

Under the IASCP, a Source Ranking Data base (SRD) is being developed to assist EPA in identifying high priority indoor air sources for further review. While the SRD is being developed, EPA began a more detailed analysis of emissions, exposures, and possible risks from latex and alkyd paints for general use on drywall and its associated wood trim. Wall paint was chosen because greater emissions are expected to arise from liquid products and large quantities of these paints are used frequently during construction and renovation. It was agreed upon in a joint management meeting that the OPPT existing chemicals program (ECP) Risk Management (RM1 and RM2) process would be the mechanism for the evaluation of risk and development of risk management options for the Wall Paint Case. The RM1/RM2 process as developed for cluster cases would be followed with some notable exceptions: all decision meetings will include appropriate management from ORIA and OPPT; ORD staff would be called upon for technical advice; and stakeholder's meetings would have representatives from all offices involved. Due to the presence of biocides in paint that may degrade and release formaldehyde and possibly other chemicals, the Office of Pesticide Programs (OPP) has become involved in this project.

1.1 Purpose of this Report

This report is a screening level risk assessment of wall paint for the RM1 Existing Chemicals Program. Its purpose is to evaluate the many studies on wall paint to determine if there are enough concerns or potential risks associated with the exposure of consumers and workers who use wall paint indoors to warrant further work. Since this is a screening level exercise, much of the analysis is qualitative. However, rough quantitative estimates of risk are given for those chemicals that have quantitative hazard data and readily available monitoring or chamber concentration data. This analysis will be used to determine the possible disposition of this case. Possible

outcomes of an RM1 analysis include: (1) case enters into higher level of review (i.e., RM2), (2) case is referred to another agency (e.g., OSHA, CPSC) who has jurisdiction over the exposed population, (3) write a test rule to fill significant data gaps, and/or (4) drop the case from further review because exposure/hazard/risks of concern were not identified. The development of risk management options and a more extensive quantitative risk assessment would be done during a RM2 analysis.

1.2 Status of Report

A draft RM1 Wall Paint Dossier (dated June 28, 1995) was prepared and sent to industry for comment. During the time that industry was preparing their comments, a small chamber emission study for latex paint on wall board was completed by the ORD, Indoor Environments Branch. Dr. Bruce Tichenor was the primary researcher. Data from this study indicated that for latex paint, the wall board played an important role in the absorption of chemicals from the latex paint. This significantly impacted the screening level exposure/risk assessment completed for the draft assessment. Therefore, this final draft RM1 Dossier contains a revised exposure/risk assessment for latex paint as well as comments submitted to EPA from the paint industry through the National Paint and Coatings Association. The biocides industry also provided comments that were included in the section 2.1.5.

1.3 Summary of Interactions with Wall Paint Stakeholders and Others regarding Wall Paint

EPA has met with the paint industry on several occasions to, at first, inform them of our intention of preparing a screening level risk assessment on wall paint and then to discuss the risk assessment. Additional meetings have been held to supply industry with basic information on the small chamber test methods which supplied data for the risk assessment. These meetings were held either as part of the NPCA's Product Safety Committee meetings or at the EPA facilities at Waterside Mall in Washington, D.C. Sherwin Williams, Inc., who is not a member of the NPCA, but who is a major producer of wall paint, was invited and participated in most of the meetings.

In addition to meeting with the paint industry, EPA has met with and received comments on the draft RM1 dossier from Troy Corporation, a biocides manufacturer. Troy representatives presented small chamber data to EPA on April 26, 1996. Although, this data showed that formaldehyde was emitted by wall board and paint with and without biocides in it, the data could be not included in this Draft Final Wall Paint RM1 Dossier because of

confidentiality claims and compensability issues. It was suggested that Troy submit their data directly to the Office of Pesticide Programs where these issues could be handled.

1.4 RM1 Activities

A RM1 management decision meeting was held May 17, 1995 after the draft RM1 risk assessment was completed. Decisions made at that meeting were included in the Draft RM1 Wall Paint Dossier. While some of the decisions made at this meeting have been addressed, other decisions were revisited during a second management decision meeting held on Sept. 24, 1996 in light of the revised risk assessment and subsequent activities on wall paint. Section 7 of this final draft dossier reflect the conclusion and recommendations made at the Sept. 24, 1996 meeting.

2.0 PRODUCT DESCRIPTIONS AND USES

2.1 Chemical Components of Wall Paint

Paint is a mechanical mixture or dispersion of pigments or powders with a liquid or medium known as the vehicle. The vehicle portion of the paint normally consists of a non-volatile portion (film-former- i.e. resin and/or oil) and a volatile portion (i.e. solvent). The non-volatile portion remains as part of the paint film and the volatile portion evaporates after application of the paint, thus leaving the film (EPA 1992). In addition to the pigments and vehicles, numerous additives are employed to enhance both physical and application properties.

Wall paints can be latex (water-based) or alkyd (solvent/oil-based). The degree of gloss, or sheen, they emit further classifies them as flat (no gloss), semi-gloss, or glossy (EPA 1992). Over 85% of wall paints are water-borne and are applied by brush or roller.

Wall paints fall under the Standard Industrial Classification (SIC) end use of architectural coatings (SIC 28511). Included under architectural coatings are interior paints, exterior paints, lacquers, and other coatings formulated for normal environmental conditions and used for standard commercial, residential, institutional, and industrial applications.

2.1.1 Film-Formers

The film-former is the clear resinous material which forms the continuous medium in the dry film after solvent evaporation with or without chemical reaction (e.g., oxygenation) and/or heat. The film-former determines the major properties of the paint. Properties of a good film-former are good solubility, easy application, good adhesion, hardness, toughness, flexibility, durability, and drying speed. Film-formers should also be resistant to moisture, oxygen, light, and heat (EPA 1992).

Film-formers are based on one or more of the following: drying oils, synthetic resins, and/or natural resins. The resin classes used are alkyds for solvent-borne paints and acrylics, vinyls, and styrene butadienes (in flats) for water-borne paints. The 1990 and 1991 resin composition of wall paint based on weight is exhibited in Table 1.

Table 1. Domestic Resin Consumption in Wall Paints 1990 and 1991

Resin Type	% of Total (by weight)		Millions of Pounds	
	1990	1991	1990	1991
Acrylic	17.6%	17%	73.1	68.2
Alkyd	19.7%	19%	82	75.3
Styrene-Butadienes	3.5%	4%	14.5	14.5
Vinyl	59%	60%	245	236.6
TOTAL	100%	100%	415	394.6

Source: NPCA 1992

Alkyds are typically oil-modified polyester resins. They are formulated by a condensation reaction of polyhydric alcohols (e.g. glycerol), polybasic acids or their anhydrides (e.g. phthalic acid or anhydride), and an oil or oil acid. Alkyds used in wall paints normally are modified with large percentages of drying or semi-drying oils; such alkyds are referred to as long-oil or medium-oil. Among the desirable properties of alkyds are excellent drying, durability, gloss, and gloss retention. Alkyds also retain color and flexibility well (Weismantel 1981).

Acrylics are thermoplastic resins obtained from the polymerization or copolymerization of acrylic and methacrylate esters. When dispersed in water or organic non-solvents,

acrylics provide latex and organosol coatings, respectively (Weismantel 1981). Acrylics are used in top-line flats and in semi-gloss/gloss latexes because of good gloss and tint retention, although new technologies may reverse this trend (NPCA 1992).

Vinyls are either homopolymers of polyvinyl acetate (PVA) or copolymers of vinyl acetate and acrylic monomers. In general, interior wall paints are vinyl acrylics (vinyl acetate/butyl acrylate polymers not vinyl acetate polymers. (NPCA 1996) Water emulsions of high molecular weight polyvinyl acetate are used in wall paints, where their softness is mitigated by a high pigment content. Copolymers of vinyl acetate with acrylic monomers compete with more expensive and durable all-acrylic copolymers for use in wall paints (EPA 1992). Straight vinyl paints have a major share in latex flats because the performance requirements of such paints are less than for semi-gloss and gloss paints (NPCA 1992).

Styrene-butadiene resins are copolymers of polystyrene and butadiene, and are used in emulsion latex paints. Use of these resins is declining due to tendencies to induce brittle coatings and yellowing with age. These resins also exhibit poor freeze/thaw stability and a low critical pigment-volume concentration (Weismantel 1981).

2.1.2 Solvents

Solvents, in general, are low viscosity volatile liquid component used to improve application properties. Solvents function to:

- dissolve the film-former
- reduce the solution or emulsion to proper solids content and proper viscosity
- control the rate of non-sticky film formation by their own evaporation rate, thereby controlling the final drying cycle.

Solvents used in latex paints function primarily as coalescing aids which serve to soften and solvate the partial latex particles so that they flow together and form a continuous film, especially at lower temperatures. Table 2 lists the types of wall paint solvents and their consumption in 1991 except for water which is the major solvent used in latex paint.

Aliphatic Hydrocarbon solvents are used in alkyd paints. These solvents are generally straight-chain petroleum fractions

and may contain some aromatics. They include VM&P Naphthas, mineral spirits, hexane, and heptane. About 75% of aliphatic hydrocarbons used in wall paint are mineral spirits (EPA 1992). Aliphatic Hydrocarbons accounted for about 56% of solvent consumption in wall paints in 1991.

Ethylene glycol is the primary solvent, other than water, used in latex flats. It is also used in some semi-gloss eggshells, as well as in some latex glosses. It is expected that propylene glycol-based formulations, both latex and alkyd, will be gradually substituted for those based on ethylene glycol. While both compounds contribute roughly the same amount of VOC, formulations often require less propylene glycol than ethylene glycol. Thus, lower VOC formulations are possible using propylene glycol, although they will likely be slightly more expensive than those based on ethylene glycol (Reisch 1994). In 1991 ethylene glycol comprised 17% of the wall paints solvents market.

Table 2. Domestic Solvents Consumption in Wall Paints 1990 and 1991

Solvent Type	% of Total (by weight)		Millions of Pounds	
	1990	1991	1990	1991
Aliphatic Hydrocarbons	56.9%	55.5%	98.4	90
Ethylene Glycol	17%	17.5%	29.3	28.4
Glycol ethers/esters	7.2%	7.3%	12.5	11.8
Propylene Glycol	16%	16.6%	27.7	27
Other ketones/esters	1.2%	1.1%	2.0	1.9
Xylenes	.8%	.6%	1.3	1.1
Miscellaneous	.9%	1.4%	1.6	1.8
TOTAL	100%	100%	173	162

Source: NPCA 1992

Note: Water is the predominant solvent in latex paints.

Propylene glycol is the major organic solvent for use in semi-gloss latex wall paints. In 1991, it made up about 17% of the wall paints solvent market. Since it often can be substituted for ethylene glycol, propylene glycol will likely be used in more latex formulations over time (Reisch 1994).

Glycol ethers and esters are fully miscible with water and are vital in developing freeze-thaw stability, coalescence, and wet-edge control. These compounds are used in latex paints and are relatively volatile (EPA 1992). Glycol ethers and esters accounted for 7.3% of the solvent market in wall paints in 1991.

Alcohol and ketone & ester solvents are not used widely in wall paints. Among these are methyl ethyl ketone and methyl isobutyl ketone. Their use is limited to some semi-gloss and gloss latex vinyl paints (NPCA 1992).

Xylenes are aromatic hydrocarbons used with short-oil alkyds. Aromatics are being phased out of wall paint use due to their generally high VOC content. Formulators are under continuing pressure to reduce their use (Reisch 1994).

2.1.3 Pigments/Fillers.

Pigments are finely divided, insoluble, solid organic or inorganic particles dispersed in the coating vehicle and distributed throughout the binder in the final film. There are two major types of pigments:

- prime whites
- extender/ filler pigments

Metallic powders and colored pigments are also used (Rauch 1990).

Prime pigments contribute color and gloss as well as opacity. Opacity is the ability to obscure or hide the substrate. All else being equal, the more pigmentation the lower the gloss. Extender pigments (fillers) have much lower refractive indexes than prime pigments and contribute little to opacity. Their main function is to lower costs of the final coating and to fortify the film against cracking. Fillers are also added to contribute fullness and viscosity to paints, as well as to add some color (Rauch 1990). Table 3 lists the major wall paint pigments and their consumptions in 1991.

Titanium dioxide (TiO_2) is the largest paint prime pigment, comprising 30.5% of the pigment/filler market in 1991. TiO_2 is a very stable white pigment, soluble only in hot concentrated sulfuric acid. It is inert to all binders and resins in wall paints. It also has the highest refractive index of any pigment, which gives it the best hiding power. Since it is hydrophilic, TiO_2 may present difficulties in dispersing in oil-based paints. TiO_2 is loaded at 0.88 lb. per wet gallon (Rauch 1990).

Clay is used as a filler to enhance whiteness and help hiding. It comprised 32.8% of the domestic market in 1991. It is used widely in latex flats because their soft films reduce water resistance and thus do not hold up under more strenuous conditions (Rauch 1990).

Table 3. Domestic Pigments/Fillers Consumption in Wall Paints 1990 and 1991

Pigment	% of Total (by weight)		Millions of Pounds	
	1990	1991	1990	1991
Titanium dioxide	27.7%	30.5%	265.8	278
Calcium carbonate	14.1%	14.3%	134.8	130
Talc	13.8%	13.8%	132.4	126
Clay	33.1%	32.8%	317.5	299
Silica	5.2%	5.3%	49.9	48
Iron oxide	1.8%	1.8%	16.9	16
Others	4.2%	1.5%	40.7	15
TOTAL	100%	100%	958	912

Source: NPCA 1992

Calcium carbonate is used as an extender pigment, accounting for 14.3% of the wall paint filler/pigment market in 1991. Intermediate sizes (i.e. coarseness of the particles) are used in flat and semi-gloss paints, while ultra-fine grades are used in gloss paints to adjust consistency and minimize sagging. Calcium carbonate can reduce costs without affecting coating properties (Rauch 1990).

Talc is a form of hydrated magnesium sulfate. It serves as an excellent extender since it is readily wetted and dispersed and inhibits hard settling of other pigments. Talc also helps reduce sagging (Rauch 1990).

2.1.4 Additives

Additives are miscellaneous chemicals which are added to the paint formulation to enhance or add desired qualities such as viscosity, durability, or appearance. Additives also ease

applicability, accelerate drying, and decrease foaming, among other things. Additives generally fall into one of the following categories:

- **thickeners:** These compounds modify viscosity to control flow, pigment settlement, and leveling. Typical thickeners include cellulose ethers, micronized silica, and natural clay (EPA 1992).

- **plasticizers:** These materials are added to a formulation to maintain coating flexibility and to avoid cracking and checking, all without sacrificing film strength, continuity, and chemical resistance (EPA 1992).

- **surfactants:** These include anti-foaming agents, which prevent foam formation during application of the paint. Emulsifiers and stabilization agents are also classified as surfactants (EPA 1992).

- **driers:** Driers promote and accelerate drying of paint after application, without reacting with the vehicle (i.e. resin) components. Metals are popular driers, and the most commonly used ones for all paints include lead, cobalt, calcium, iron, manganese, and zinc. Driers for alkyd paint include cobalt, zirconium, manganese, and calcium.

- **stabilizers:** These are used to prevent water-borne coatings from coagulating or flocculating when the paints are subjected to freezing temperatures. Ethylene glycol and propylene glycol are the major freeze/thaw stabilizers used. Another method of achieving such stability is by use of an additive that improves the stability of the emulsion (Weismantel 1981).

Additives generally make up less than one percent of total paint formulation.

Note that the use of lead in paint on or used as consumer products is restricted by a Consumer Product Safety Commission regulation (Tab A, 16CFR part 1303) to a 0.06% maximum allowable limit as measured by weight in the dried paint film. Lead has occurred in paint as pigments, driers, and contaminants. Contamination is believed to be the remaining source of lead in paint, aside from manufacturing errors. Likely source of contamination are the natural presence of lead in certain pigments derived from earthen materials, for example, zinc ore, and the accidental cross-contamination of lead-free paint by intentionally-lead paint or other lead product manufacturing processes within the same facility (FR Vol. 57, No. 84, 1992).

2.1.5 Biocides

Water-based paint is an excellent growing media for microorganisms (e.g., bacteria, fungi, molds, mildew) and must have a preservative to prevent microorganisms from degrading the paint (Rauch 1990). Oil-based systems with less than 5% water, in general, do not require an in-can preservative. The draft RM1 Dossier for Wall Paint listed 96 antimicrobial chemicals (biocides) that were classified by EPA/OPP as preservative or fungicide that had been used in paints (Dang 1995). NPCA stated in their comments on the draft RM1 Dossier that many of the 96 antimicrobial chemicals that are listed are not used by the industry. A similar comment was made by the Adrian Krygsman of the Troy Corporation, a biocide manufacturer. Therefore, Appendix A of this final draft report has been revised using strikeout format for those chemicals that were removed from the list by Troy, Corporation. Historically, mercury-containing compounds have served as preservatives and are still listed on the master list (Appendix A), however, EPA outlawed their use in paints in 1991 and other compounds on the list are being used in its place.

In addition to preventing growth of microorganisms in the can, preservatives are formulated into paint to reduce growth on the walls that are being painted. Many homes and buildings have areas of high humidity/moisture, such as, bathrooms and kitchens, where mildew is a recurring problem. Consumers may seek out specific paint products that have components that prevent the growth of mildew. Of the chemicals listed in Table 4, 45 have been identified as being used as preservative for applied films, 80 chemicals were identified as being used as in-can preservation, and 6 chemicals have been used over paint films and the surfaces they cover. After removal of those biocides that industry claim are no longer used in paint, there are 23 preservatives listed for applied films, 55 as in-can preservatives, and 4 are used over paint films and the surfaces they cover.

Each active ingredient has its own recommended treatment levels, but the average value of in-can preservative concentration ranges from 0.05% to 0.5% (500 to 5,000 ppm). Industrial antimicrobials are expensive components of product formulations and it is therefore in the manufacturers' best interest to optimize the amount used versus the protection provided.

2.1.6 Wall Paint Constituent Data Sources

Information on the chemicals used in wall paint was found in several sources and each source had its limitations as to the quality and extent of the data it contained. Sources which contain formulations data and analytical data were used to develop the table of paint chemical constituents. Both types of data are important in order to get information on the chemicals formulated into wall paints as well as those chemicals that are degradation products (e.g., formaldehyde and acetaldehyde). Appendix B provides summary information on the wall paint chemicals identified from the major data sources.

The analytical studies varied in their methodologies and scope. Some of the analytical studies tested only one or two brands of paint. Another study tested a paint that was specifically made for that study. Some of the constituent data are from analysis of bulk samples, while other data were collected from the air in small stainless steel chambers or in dormitory rooms. The two small chamber studies varied as well.

The RTI study used only glass slides to apply the paint to, while the EPA/ORD study uses both glass slides and wall board (i.e., dry wall) as the applied surface (the substrate). The data that were most valuable for the screening level risk assessment came from the studies that mimic exposure most closely, that is, the ITC study (#1 below), the EPA/ORD study (#5 below), and the RTI study (#6 below). Formulations data were not used to generate model estimates of exposure in this RMI assessment. The major data sources used to develop Appendix B are described below:

1) Exposure to Volatile Components of Polyvinyl Acetate (PVA) Emulsion Paints During Application and Drying.

Date: 2/14/92

Author: Prepared by ITC for the National Paint and Coatings Association

Document seeks to characterize exposure to the primary VOC emitting chemicals of interior latex polyvinyl acetate (PVA) paint during typical application conditions. Polyvinyl acetate is one of the major resins (film-formers) used in latex paint. Those chemicals studied were formaldehyde, vinyl acetate monomer, acetaldehyde, butyl acrylate, ethylene glycol, and Texanol (2,2,4-trimethyl-1,3-pentanediol monoisobutyrate).

The primary purpose of the study was to determine potential worker and consumer exposure to volatile components (e.g., vinyl acetate monomer) during field application of PVA paint and to evaluate factors contributing to such exposure. Exposure data were collected during application of paint with airless spray equipment and roller/brush combination in two ventilation scenarios (0.5 and 5.0 air exchanges per hour). The study was conducted in a series of similar dorm rooms at a university residence hall during the summer while the rooms were unoccupied. Air samples were collected and tested at beginning and during application, as well as at intermittent periods after application.

All dorm rooms were painted using the same PVA paint. This paint was specifically formulated by a NPCA member to contain 3000 ppm of vinyl acetate monomer (VAM). NPCA considers this level of residual VAM to be representative of commercially available resins currently used to formulate PVA emulsions. However, NPCA in their comments on the draft RM1 Dossier for Wall Paints, stated that they believe the residual vinyl acetate monomer levels in PVA resins are "trending downward", although no levels were given. The downward trend is reported to reduce the potential for acetaldehyde exposure (NPCA 1996). Since no new levels are available the results provided in the ITC study are used to estimate exposure and risks.

2) U.S. Paint Industry Database.

Date: 9/92

Author: Prepared by SRI for NPCA

Provides a statistical database for the paints and coatings industry. The report contains four levels of production and consumption data, including:

1. Basic raw materials
2. Industry raw materials
3. Formulated coatings
4. End-use markets

The data are used for assessing (a) the impact of the paints and coatings industry on its raw materials suppliers, its customers, and the economy in general, and (b) the impact of these segments on the paint and coatings industry.

3) Interior Architectural Coatings Market Study.

Date: 9/30/92

Author: Prepared by Mathtech, Inc. for EPA

Report provides profile of the Interior Architectural Coatings industry. The report analyzes paint types and uses, major functional constituents of paints, differences in formulations, market shares and consumption patterns, substitutes, government regulations, and technological trends.

4) Draft Interim Report Volume II, Architectural and Industrial Maintenance Surface Coatings VOC Emissions Inventory Survey.

Date: 2/2/93

Author: Industry Insights for NPCA

Emissions survey lists HAP chemicals sorted by use category and VOC range. The survey also lists the survey incidence of these HAPs within each use category.

5) Latex Paint Emissions.

Date: 8/94

Author: EPA/Air and Energy Engineering Research Lab, Dr. Bruce Tichenor, primer researcher; Acurex, primer contractor.

Part I. Initial Assessment- Data summary.

This part summarizes experimental data collected on the test product (Sherwin Williams Class 99 Interior Flat Latex Paint- Dover White 112-4460, which contains 83 mg VOC per gram of paint, or 8.3% VOC by weight.) and provides results of initial small chamber scouting experiments. Results are given for (a) VOC emissions after application to gypsum board and stainless steel plate, (b) comparisons between first and second coats, and © comparison with another brand of latex paint.

Part II. Static and Dynamic Chamber Testing and Modeling of Emissions- Draft Final Plan

This plan describes the technical approach to Phase II, which will consist of testing to collect data for development of models to predict emissions of VOCs from latex paint.

6) Determination of Test Methods for Interior Architectural Coatings.

Date: 5/13/94

Author: RTI for EPA

This study is a follow-up to a previous study which evaluated seven methods for determining VOC emissions from Interior Architectural Coatings. This study provides detailed evaluation of three of those methods:

1. ASTM methods- VOCs by % weight in samples.
2. Bulk product analysis- GC/MS analysis for mg/g VOC.
3. Small chamber testing- air conc. (mg/m³), applied to various models to get emission parameters for target VOCs, TVOCs, and aldehydes.

Study methods description, analytic results, quality assurance/quality control results, method evaluation results, and method comparisons are given for latex and alkyd paints. Testing was performed on 10 brands of each type of paint to insure broad range of gloss types and colors.

2.1.7 Regulatory Status of Individual Chemicals (except biocides)

The regulatory status of each chemical identified as being in wall paints was obtained from the Screening Information System on the Local Area Network (SIS/L). SIS/L is an interactive, LAN-based system that serves as a pointer to over 20 databases and chemical lists. The sources referenced in SIS/L contain information on chemical toxicity, exposure, and regulatory status. Most of the lists and databases in SIS/L are related to EPA regulatory programs. A few key information sources from other agencies are also included. Appendix C is the output provided by SIS/L search done prior to June 1995.

2.2 WALL PAINT APPLICATIONS

In general latex paints are used in preference to alkyd paints indoors because they release much less odor, cost less, dry faster and are easier to clean up. Alkyds function indoors primarily in high-gloss applications or when a particular substrate or condition necessitates their use. Such a substrate might be metal, plastic, wood, or glass. A condition, for example, a high moisture area where mold growth has been a problem, such as kitchens and bathrooms, may prompt a consumer to choose alkyd paint for the gypsum wall board in these areas.

2.2.1 Flats

Comprising 70% of the wall paint market, flats are by far the most widely used type of wall paint. These paints are designed for "low traffic" areas such as living rooms, dining rooms, bedrooms, or any other such area. They can be applied to drywall (gypsum board), plaster, wood, and masonry. Due to their relatively low hardness, they do not hold up well to continued washing and should not be used in higher moisture areas, such as bathrooms, basements, and kitchens.

2.2.2 Semi-gloss

Semi-gloss paints may be used in traditionally low-traffic areas where one anticipates more activity (i.e. living rooms, dining rooms, bedrooms), as well as higher traffic areas where one might expect more than normal activity, such as hallways and walls along staircases. They are also used on ceilings, where moisture tends to collect, as well as in other traditional high-moisture areas such as bathrooms, kitchens, and basements.

2.2.3 Gloss

Gloss paints are typically used outdoors where environmental conditions are harsher. Gloss paints tend to release more odor making them more unpleasant indoors. However, they can be used in very high-moisture areas of a building, or areas which are subjected to particularly stringent chemical conditions (e.g. salt). Gloss paints are also used for trim woodwork along floors, ceilings, windows, and door frames.

3.0 CONSUMPTION DATA AND MARKET TRENDS

3.1 Consumption

Approximately 229 million gallons of interior wall paints were consumed in 1991. Of this amount, 203 million gallons (89%) were water-born paints, and 26 million gallons (11%) were solvent-born (NPCA 1992). Sales have increased steadily for the past decade and are expected to grow by 2%-3% over the next five years (Mullin 1994). Sales in the architectural coatings market as a whole grew 5.5 percent in the first half of 1994, with similar growth projected for the remainder of the year. Table 4 shows the U.S. wall paint consumption from 1987 to 1991 (NPCA 1992).

Table 5 shows a breakdown of wall paint consumption in 1991. In 1991 latex flats comprised 97% of all flat wall paints. Latex

semi-gloss comprised 75% of all semi-gloss wall paints, while latex gloss only comprised between 5% and 7% of gloss wall paints. In 1973, latex flat and latex semi-gloss wall paints comprised 90% and 45% of the flat and semi-gloss wall paint market, respectively. In 1981, those figures were 93% and 70%, respectively (NPCA 1992).

Table 4. Domestic Wall Paints Consumption Over Time

Year	Flats(MM gal)		Gloss and Semi-gloss (MM gal)		Total(MM gal)		% of Total	
	Latex	Alkyd	Latex	Alkyd	Latex	Alkyd	Latex	Alkyd
1981	129	10	39	24	168	34	83%	17%
1987	156	8	48	26	204	34	86%	14%
1988	157	7	48	26	205	33	86%	14%
1989	158	6	49	25	207	31	87%	13%
1990	160	5	52	24	212	29	88%	12%
1991	154	4	49	22	203	26	89%	11%

NA- Not Available

Source: U.S. Paint Industry Database 1992

Table 5. Breakdown of Domestic Wall Paint Consumption 1991

Paint Type	% of Flat	% of Semi-Gloss	% of Gloss	% of all Wall Paints
	MM gall.	MM gall.	MM gall.	Total
Latex	97%	75%	5%-7%	89%
	154	NA	NA	203
Alkyd	3%	25%	93%-95%	11%
	4	NA	NA	26
Total	100%	100%	100%	100%
	158	NA	NA	229

NA- Not Available

Source: U.S. Paint Industry Database. 1992

3.2 Market Trends

At present the paints and coatings industry is relatively healthy, as both product sales and revenues are increasing. While paint material costs declined almost 4% in 1990 and 1992, recently price increases for chemicals used in paint have increased raw materials (i.e. resins, pigments, additives) prices, a trend that worries many industry sources.

In recent years formulators have curtailed employment to keep costs down. Thus paint price increases have been relatively small. In 1993 and 1994, however, employment has been bolstered to keep up with increased demand for paint. The increased demand, along with the rising raw materials prices, makes a price increase for paints likely in the near future.

A future price increase for wall paints will also be driven by the pending VOC regulations. While new formulations are being developed to comply with lower VOC standards, many suppliers are reluctant to market them because of their lower performance capabilities. Due to the intense competition in the industry, and the fact that raw material costs make up most of the price (labor costs are less than 3% of price), many suppliers are under great pressure (Mullin 1994). At a meeting with EPA on May 13, 1996, an industry representative stated that the labor costs given above are no longer valid, however, a reference or value was not given.

The consumer paints and coatings industry has also been consolidating heavily in the past few years due to collapse of smaller firms, who cannot afford the costs of reformulating under impending VOC regulations. There are believed to be roughly 800 producers in the architectural coatings market today, in contrast with about 1300 ten years ago (Reisch 1994). Table 6 lists the top ten wall paints producers in 1989. One industry source estimates that while 10 years ago the top ten paints and coatings manufacturers made up 40% of the market; in 1994 that figure is over 60% (Reisch 1994).

3.3 Regulatory Environment

Impending national regulations and current State regulations limiting allowable Volatile Organic Compound (VOC) emissions from paints will ensure the continued general trend towards water-borne (latex) paints for indoor architectural coatings. Since 1987, California, a proxy for future environmental trends, has prohibited sales of flat and non-flat architectural coatings which contain more than 250 gm/l. Similar legislation exists in New York, New Jersey, Texas, and Arizona (NPCA 1992).

On June 18, 1997, the U.S. EPA proposed a national regulation to control volatile organic compound (VOC) emissions from architectural coatings. Although EPA and the major stakeholders were unable to reach a negotiated conclusion in regulatory negotiation process, the information obtained from these discussions was useful in developing the proposed rule. EPA's proposed rule will set a VOC content level for 55 categories of architectural coatings and would reduce emissions of VOCs by 106,000 tons per year, representing a 20 percent reduction from 1990 levels. VOC limits for flat and nonflat interior paints would be 250 and 380 g/liter, respectively. It is expected that the final regulation will be sent to the Office of Management and Budget in August 1997 and that compliance date will be Jan.1, 1998.

Table 6. Top Ten Producers of Wall Paints

PRODUCERS	PERCENT SHARE (1989)
Sherwin-Williams	15.9
ICI (formally Glidden)	13.2
Benjamin Moore	7.4
PPG Industries	6.4
Desoto	3.8
Kelly-Moore Paint Co.	3.7
Valspar	3.6
Grow Group	3.4
Pratt & Lambert	3.0
Porter Paint/Courtaulds	2.2
TOP TEN COMPANIES	62.8
OTHER COMPANIES	37.2

Source: EPA 1992

4.0 TECHNOLOGICAL TRENDS

4.1 Resins

The EPA's focus on VOC emissions is forcing many formulators to employ otherwise unused resin technologies aimed at reducing VOC emissions to the point of zero emissions. Ultimately, an industry goal is to commit to achieving 100% solids, no solvent, zero-emissions formulations. Recent U.S. procurement and development of "no-VOC" technology in resins for latex paints is cause for some optimism. These efforts are summarized below.

4.1.1 Technical Summary

Interior latexes are usually not considered to be in the same category as alkyd paints because they can be cleaned with water, are non-flammable, and usually produce less odor than alkyds. But latexes nevertheless contain volatile and semivolatile organic chemicals (as defined by vapor pressure not the Clean Air Act definition) in the range of 3.5- 9.5% (RTI 1994) simply to achieve certain desirable properties. Total elimination of VOCs from latex paints is not possible if "no-VOC" is defined as below detectable limits. This difficulty results because latex polymers are produced through polymerization of relatively volatile organic monomers, and so small, detectable amounts of residual monomer remain present in the final emulsion product. As mentioned before, NPCA believes that levels of residual vinyl acetate monomer of 3000 ppm, which was considered representative of commercially available resins, are now trending downward although no levels were given. Eliminating VOCs from latex paints without completely reformulating the paints would impair the properties of the paint or make it completely unusable.

Vinyl acrylics are the most commonly used latex binders because of their low cost and versatility. But these systems require the use of coalescing aids (solvents) to achieve certain performance properties. Coalescing aids comprise roughly 2% of latex formulations and are a major source of volatile organics in latex paints (Klein 1993). Thus, efforts to further reduce volatile organic content of latex paints must concentrate on elimination of coalescing aids while maintaining the properties achieved by them. These properties include pigment acceptance, low-temperature film formation, scrub resistance, and cost effectiveness (Klein 1993). In general, lowering the film-forming temperature has required the use of more solvent.

In order for a binder to be able to form a film at low temperatures, it needs to exhibit a relatively low glass transition temperature (T_g). Normally a binder needs to exhibit a minimum film-forming temperature (MFFT) or T_g of about 5 degrees C. Paints based on vinyl acetate copolymers possess a distinct advantage with regard to film formation at low temperatures because they are subject to hydroplastication during drying. Water acts as a plasticizer or softener for the copolymer, which allows the binder to form a film at temperatures below their glass transition temperatures. This feature is in contrast to most other polymer systems, which only form films at degrees above their glass transition temperatures. Thus, vinyl acetate copolymers have an advantage with regard to the elimination of coalescing aids. This advantage is evident in their scrub resistance and lack of blocking (Ulyatt 1993).

Experience in Europe, where solvent-free formulations were first developed, has shown that polymers based on ethylene exhibit the best properties. One survey covering 26 solvent-free paints in Europe found 18 to be based upon vinyl acetate ethylene copolymers. This ratio is much higher than that exhibited for the same polymers in the total European market (Ulyatt 1993).

One expert believes the performance viability of the new polymers has resulted from steady increases in the molecular weight of the polymers produced, which improves their toughness and lack of stickiness. Further improvements in the use of functional monomers has facilitated adhesion of the films to difficult surfaces. These advances have reduced the need for coalescing aids in formulating latex paints (Ulyatt 1993).

A key feature which ensures the marketability of solvent-free latex paints is their lack of odor. Normal binders contain about 2000 ppm (parts per million) of VOC, mainly residual vinyl acetate monomer. The new paints contain less than 200 ppm of VOC, with vinyl acetate reduced to roughly 50 ppm. These lower levels of VOC result in much less odor than that emitted by conventional paints. The low odor is achieved not only through the use of the new polymer technology, but also through careful selection of other raw materials and mixtures. Among those other chemicals whose use is now kept to a minimum is formaldehyde (Ulyatt 1993). At a meeting with industry on May 13, 1996 with EPA, an industry expert stated that the presence of formaldehyde in this category of products is largely to residual (trace) contamination. Typical values of formaldehyde in latex resins are less than 0.05% by weight. Another source of formaldehyde in latex paint is biocides. Although formaldehyde is not directly formulated into latex paint, 21 of the biocides listed in table 4 for in-can preservation are "formaldehyde donor" types which continue to be important to the industry (NPCA 1996). Small chamber test data presented at a meeting of the EPA wall paint workgroup and Troy Corporation representatives on April 26, 1996 showed that although formaldehyde was detected in the wall board and paint without biocides, paint with certain biocides contained the higher levels (EPA 1996).

Another feature of new resin technology is that paints formulated with it do not require the additional use of glycols to achieve freeze/thaw stability. Glycols not only serve to achieve temperature stability, but are also used to disperse colorants. Colorants are generally available at low-VOC levels, but the added cost is significant (Klein 1993). Since the new technology can be applied to no-glycol containing paints, one can choose an alternative color no-VOC paint without having to purchase tints.

4.1.2 U.S. Application

No-VOC paints have been commercially available in Europe for some time. Recently, however, U.S. firms have obtained or begun to develop similar technology to formulate latex paints with virtually no volatile organics. Three notable examples are Rohm and Haas' Rocace SF-091/Rhoplex SF-012, Nacan Products Limited's Vinamul 3692, and Air Products Limited's Airflex 738.

1. Rohm and Haas- Rocace SF-091/Rhoplex SF-012

No-VOC latex paints first became commercially available in the U.S. in 1992, when Glidden introduced its Spread 2000 and Lifemaster 2000 brands. Both paints utilize a water-borne polymer system developed by Rohm and Haas, and are available in flat and semi-gloss formulations. These polymer systems are trade-named **Rhoplex SF-012** (semi-gloss and satin) and **Rocace SF-091** (flats). Rohm and Haas claims that paints based on these binders display all the key performance characteristics associated with more conventional latex paints. Reportedly, paints using Rhoplex SF-012 emit no odor minutes after application, and those formulated with Rocace SF-091 are odorless one hour after application (Rohm & Haas Resin Review 1992). Color for these paints is limited to off-white, although tints containing less than 40 grams per gallon of VOC can be purchased to add color. The price of these paints is \$18.99/gallon (1992\$), in comparison to an average price of \$20.50/gallon for those in a representative sample of latex paints, as surveyed by Consumer Reports in 1991. (EPA 1993)

2. Nacan Products Limited- Vinamul 3692

Nacan Products Limited (Canadian affiliate of National Starch, Unilever's U.S. chemicals operation) has employed European polymer technology to develop **Vinamul 3692**. Vinamul 3692 is a line of ethylene vinyl acetate terpolymer emulsions which can be used to formulate both flat and semi-gloss paints. Nacan has tested a 27% PVC semi-gloss paint, a 37% PVC eggshell paint, and a 62% PVC flat paint, all formulated with no coalescents or glycols. All three paints exhibited equal or better performance with regard to scrub resistance and gloss retention when compared to commercially available solvent-free paints (Modern Paint and Coatings 1993). Vinamul 3692 differs from the Glidden technology in that it does not necessitate the use of tints to achieve colors other than white. Thus, one's choice of a different color does not require the addition of VOC containing tints. Vinamul 3692 is manufactured in Woodruff, South Carolina.

Nacan also manufactures two all-acrylic emulsions, Nacrylic 2592 for semi-gloss paints and Nacrylic 2792 for eggshell paints, which can produce VOC-free coatings. These emulsions are manufactured in Canada (Reisch 1994).

3. Air Products and Chemicals, Inc- **Airflex 738**

Airflex 738 is a terpolymer of vinyl acetate, vinyl chloride, and ethylene. The company claims that scrub resistance and durability are superior to other conventionally formulated paints. In addition, the system is characterized by a fine particle size, which not only helps in low temperature film-formation, but provides excellent pigment binding properties as well. Airflex 738 is also touted as enabling producers to formulate no-VOC paint with freeze/thaw stability, without the use of glycols. (Klein 1993)

Paints formulated with Airflex 738 to pH values of over 8.5 requires the use of a base or buffer. While fugitive bases (e.g.. ammonia, amines.) provide better water resistance, they contribute volatile organics to the final paint. To attain the lowest VOC and odor levels, Air Products recommends the use of a permanent base such as potassium carbonate. (Klein 1993)

The examples of Glidden and European manufacturers make it obvious that veritable "no-VOC" latex paints can be formulated. These paints perform similarly to more conventional paints and can be marketed at prices comparable to more conventional paints. Until such paints achieve a strong market hold, they should find most of their use in hospitals, schools, and other indoor places which cannot afford to shut down while paint dries and odors disappear. The long-term likelihood that these paints will gain a larger market share depends on two things:

- The ability of manufacturers (esp. smaller ones) to attain the technology required to achieve such formulations. This could occur through licensing of existing technology or formulation of new technology.
- The "marketability" (i.e. attractiveness) of "no-VOC" paint. The novelty of such paints and apprehension concerning their performance may prevent them from being widely used in the short-term.

4.2 Chemical Substitutions and Other Technologies

4.2.1 Chemical Substitutions for Latex Paint

Surfactants as replacements for coalescing aids

Some surfactants can replace some coalescing solvents in latex paints. ICI (Glidden) has developed a very low-VOC specialty surfactant, Pycal 94, which can replace up to half of high-VOC coalescents. The result is a latex paint with a VOC level as low as 0.5 lb per gallon. (Reisch 1994) However, performance of such paints is not likely to match that of conventional paints. Use of surfactants tends to increase the water sensitivity of the film, which then decreases its scrub resistance. In addition, use of many surfactants causes them to leach to the surface of the film, which induces haziness and discoloration.

4.2.2 Chemical Substitutions for Alkyd Paint

Surfactants as replacements for solvents

Alkyd resins generally require the use of many solvents. However, ICI (Glidden) has developed a surfactant, Atlas G-3969, to emulsify alkyds in water. This surfactant may be added at 5% to 10% by weight to the resins. ICI claims the contribution to VOCs of this surfactant is much lower than that from a conventional paint. Currently this resin is used for industrial purposes, and its high cost may preclude it from being used in more sensitive markets like wall paints (Reisch 1994).

Linseed Oil as a Substitute for Petroleum-Based Solvents

Modified linseed oil has been found to be a viable substitute for petroleum-based solvents used in alkyd resins, according to a scientist for Cargill, Inc. Trade-named **Dilulin**, the substance is formulated by reacting linseed oil with cyclopentadiene. It can be substituted for solvents without sacrificing performance characteristics like hardness, drying time, adhesion, gloss, and viscosity, according to Cargill. Use of the product would avoid the need to reformulate each product on an individual basis, since Dilulin can substitute for solvents in a variety of coatings. Cargill says Dilulin is compatible in all proportions with long oil alkyds and oil modified urethanes, and can be incorporated up to 40 percent in medium oil alkyds and 15 percent in short oil alkyds (CMR 1994). Dilulin increases the solids content of the coating, and this thick coating takes longer to cure than conventional alkyd paints (Reisch 1994).

4.2.3 Other Technologies for Coatings

The following alternative paint technologies paint do not have widespread applicability for wall paints for various reasons. These may include price, difficulty of application, performance limitations, and availability.

Powder Coatings. These systems have a coating composition which is in the form of a powder. They are composed of resins and curing agents compounded with pigments, fillers, and other additives. No organic solvent or water is needed during either manufacture or application. Powder-based coatings are applied using special equipment, which presents problems for normal, everyday use. Performance of powder-based paints is also somewhat limited. Nevertheless, use of powder coatings has increased significantly in the past 10 years (NPCA 1992).

Radiation Curable Systems. Refers to compositions formulated to be cured by high-energy radiation systems, such as UV or electron beams. Their use is limited mainly to flat, non-metallic substrates like paper, wood, or plastics (NPCA 1992).

5.0 SUMMARIES OF HUMAN HEALTH HAZARD AND EXPOSURE DATA

5.1 Summary of Human Health Hazard Data

In general, a RM1 review for cluster cases relies on a screening-level hazard assessment that is accomplished by collecting toxicity data from readily available sources such as the IRIS and HEAST databases, etc. If no data exist for a chemical, a hazard score (high, medium, low) may be assigned based on structure activity relationships. In addition to completing a screening level review for all chemicals in IRIS and HEAST for this case, other data, such as TSCA Section 4 human hazard data were reviewed for certain chemicals (e.g., methyl ethyl ketoxime, C9 aromatic hydrocarbons, etc.) as well. Tables 7 and 8 summarizes the readily available toxicity information taken from IRIS and HEAST for the 85 chemicals identified as being present in alkyd and latex wall paint, respectively. Both cancer and potential human systemic toxicity benchmark values (e.g., slope factors, RfCs, etc.) are listed when available. Irritation rankings are taken from work done for the Source Ranking Data Base (Geomet 1997).

Below are listed some general observations and summaries of individual chemical toxicities:

- Of the 85 chemicals identified as being in latex and alkyd wall paint, eight were ranked as high concern according to the "high, medium, low" hazard scoring criteria employed in the Use Cluster Scoring System (EPA 1993). The hazard scoring criteria are presented in Appendix D. Hazard scores were based on existing Agency evaluations such as RfC values and carcinogen assessments when available. In the absence of readily available hazard data, scores were based on structure-activity predictions of toxicity. The high concern chemicals are listed in Table 9.
- 46 of the 84 chemicals ranked as medium concern. These are listed in Table 10.

Table 7. Hazard Benchmarks from IRIS and HEAST of Chemicals in Latex Paints

Chemical Name	CAS#	Inh. RfC (mg/m ³)	Oral RfD (mg/kg /day)	Unit Risk (ug/m ³) ⁻¹	Slope Factor (mg/kg/ day) ⁻¹	Irritation Rating	
						Dermal	Eye
Acetaldehyde	75-07-0	0.0090		2.20e-06		1	3
Acrylonitrile	107-13-1	0.0020		0.0001	0.5400		
Ammonium hydroxide	1336-21-6						3
Benzaldehyde	93-98-1		1.0000				
Butadiene	106-99-0			0.0003			
2-(2-Butoxyethoxy) ethanol	112-34-5						3
1-(3-Chloroallyl)- 3,5,7-triaza-1- azoniaadamanatane	4080-31-3					1	
Diethylhexyl phthalate	117-81-7		0.0200		0.0140		
Diethyl adipate	103-23-1		0.6000		0.0012	1	1
Ethyl acrylate	117-81-7				0.048*	1	1
Ethyl benzene	100-41-4	1.0000	0.1000			1	3
Formaldehyde	50-00-0		0.2000	**	0.0450	3	3
Hexylene glycol	107-41-5					2	3
Methyl methacrylate	80-62-6		0.08*				
Propylene glycol	57-55-6		20.000			2	1
Styrene	100-42-5	1.000	0.200			2	3
Toluene	108-88-3	0.40	0.200			2	
Vinyl acetate	108-05-4	0.20	1.0000				1
m-Xylene	108-38-3		2.0000			3	3
o-Xylene	95-47-6		2.0000				

CAS# = Chemical Abstract Number

Inh. RfC = Inhalation Reference Concentration in milligrams per cubic meter

Oral RfD = Oral Reference Dose in milligrams per kilogram per day

"*" indicates unverified value from HEAST

*** IRIS unit risk is 1.3e-05; EPA has also calculated alternative unit risk values based on PBPK models.

Table 8. Hazard Benchmarks from IRIS and HEAST for Chemicals in Alkyd Paints

Chemical Name	CAS#	Inh. RfC (mg/m ³)	Oral RfD (mg/kg/day)	Unit Risk (ug/m ³) ⁻¹	Slope Factor (mg/kg/day) ⁻¹	Irritation Rating	
						Dermal	Eye
trans-decahydro naphthalene	91-17-8					2	1
Magnesium silicate (talc)	14807-96-6					1	
Methanol	67-56-1		0.5000				
Methyl ethyl ketone	78-93-3	1.0000	0.6000			2	
4-methyl-2-pentanone (methyl isobutyl ketone)	108-10-1	0.08*				1	3
Phthalic anhydride	85-44-9		2.0000				
Styrene	100-42-5	1.0000	0.2000			2	3
Toluene	108-88-3		0.2000			2	
		0.4000					
Triethylamine	121-44-8	0.0070				1	3
m-Xylene	108-38-3		2.0000			3	3
o-Xylene	95-47-6		2.0000				

CAS# = Chemical Abstract Number

Inh. RfC = Inhalation Reference Concentration in milligrams per cubic meter

Oral RfD = Oral Reference Dose in milligrams per kilogram per day

"*" indicates unverified value from HEAST

Table 9. Chemicals Rated High Based on Available Data or SAR

LATEX PAINT	ALKYD PAINT
Acrylonitrile (107-13-1)	Chromium compounds (7440-47-3)
Butadiene (106-99-0)	Dimethyl aminoazobenzene (60-11-7)
Di(phenylmercuric) dodecyl succinate (24806-32-4)	Lead compounds (7439-92-1)
Phenylmercuric acetate (62-38-4)	
Phenylmercuric oleate (104-60-9)	

Table 10. Chemicals Rated Moderate Based on Available Data or SAR

LATEX PAINT	ALKYD PAINT
Acetaldehyde (75-07-0)	Carbon black (1333-86-4)*†
2-amino-2-methyl propanol (124-68-5)	Cobalt 2-ethylhexanoate (13586-82-8)
Ammonium hydroxide (1336-21-6)	Cobalt naphthenate (61789-51-3)
Antimony compounds (7440-36-0)	n-Decane (124-18-5)
2-(2-Butoxyethoxy)ethanol (112-34-5)	2-Ethyl toluene (611-14-3)
2-(2-Butoxyethoxy)ethyl acetate (124-17-4)	3 & 4-Ethyl toluene (622-96-8)
t-Butyl alcohol (75-65-0)	Kaolin (1332-58-7)*
Butyl acrylate (141-32-2)	Manganese naphthenate (1336-93-2)
Carbon black (1333-86-4)*†	Methyl chloroform (71-55-6)
1-(3-Chloroallyl)-3,5,7-triaza-1-azoniaadamantane (4080-31-3)	Methyl ethyl ketone (78-93-3)
Dibutylphthalate (84-74-2)	Methyl ethyl ketoxime (96-29-7)
Diethylene glycol (111-46-6)	Methyl isobutyl ketone (108-10-1)
Diethyl adipate (103-23-1)	Nonane (111-84-2)
Diethyl phthalate (117-81-7)	Phthalic anhydride (85-44-9)
Dipropylene glycol (110-98-7)	Silica (7631-86-9)*†
Ethyl acrylate (140-88-5)	Styrene (100-42-5)*
Ethyl benzene (100-41-4)	Talc (14807-96-6)*†
2-Ethylhexyl acrylate (103-11-7)	Toluene (108-88-3)
Formaldehyde (50-00-0)	Triethylamine (121-44-8)
Hexylene glycol (107-41-5)	1,2,3-Trimethylbenzene (526-73-8)*
Kaolin (1332-58-7)*	1,2,4-Trimethylbenzene (95-63-6)*
Methyl methacrylate (80-62-6)	1,3,5-Trimethylbenzene (108-67-8)*
Nickel compounds (7440-02-0)	o-Xylene (95-47-6)*
n-Propyl benzene (103-65-1)	mixed Xylene (108-38-3)*
Silica (7631-86-9)*†	
Styrene (100-42-5)*	
Talc (14807-96-6)*†	
1,2,3-Trimethylbenzene (526-73-8)*	
1,2,4-Trimethylbenzene (95-63-6)*	
1,3,5-Trimethylbenzene (108-67-8)*	
Vinyl acetate (108-05-4)	
Vinylpyrrolidinone (88-12-0)	
o-Xylene (95-47-6)*	
mixed Xylene (108-38-3)*	

* Chemical is in both latex and alkyd paint, so they are double listed, but only counted once in total count.

†Hazard concern is only for dust inhalation.

5.1.1 Comments on Hazard Rankings:

- Lead compounds are listed as an additive in alkyd paint, however, lead was banned by the Consumer Product Safety

Committee (CPSC) from paints meant for sale to consumers, used in residential housing and schools and on furniture, toys and other items meant for use by children under the Lead Based Paint Poison Prevention Act (LBPPPA), 42 U.S.C. 4801 et seq. Subsequent laws that have reduced the levels of lead even further (Tab A, 16 CFR part 1303). It is felt that the use of lead in interior wall paints subject to review under this project fall under the CPSC ban, therefore the lead-containing compounds are dropped from further review.

- Chromium compounds are listed as a pigment in alkyd paint. It is not clear what form the chromium compounds are in. Compounds where chromium is bioavailable is of concern for oncogenicity, neurotoxicity, developmental, liver and kidney toxicity. Overall, the concern is high.
- Antimony compounds are listed as an pigments in latex paint. It is not clear what form the antimony is in. Any compound where antimony is bioavailable is of concern for chronic effects, irritation, cardiovascular and reproductive effects. Humans exposed to antimony have developed pneumoconiosis. Overall, the concern is moderate
- Silica and talc are not absorbed into the body by any route. The concern for silica and talc is that they will persist in the lung causing fibrosis and silicosis. Since this assessment is not concerned with the manufacture of paint nor with the sanding of painted surfaces where this route of exposure is possible, silica and talc are dropped from further review.
- The mercury-containing compounds listed have been deleted from further consideration under this assessment because the use of mercury-containing compounds in interior paint has been banned since these data were collected.

5.1.2 Irritation Hazard

A number of chemicals found in wall paint present a high concern for skin or eye irritation at certain concentrations. Chemicals that can present high concern include alcohol and aromatic hydrocarbon solvents commonly used in alkyd paints and aldehydes emitted from latex paints. EPA has developed a quantitative assessment of the irritant effects of formaldehyde (USEPA 1987). Acute irritant effects of formaldehyde include eye irritation beginning at about 0.1 ppm in some people and nose and throat irritation beginning at about 1 ppm. Formaldehyde can also cause chronic irritation effects. Mucociliary inhibition

and squamous metaplasia were observed in workers exposed for several years to formaldehyde in the range of 0.1 to 1.1 ppm. The mucociliary system is an important defense mechanism in the removal of foreign particles and bacteria that enter the upper respiratory system. A reduction in the efficiency of this defense mechanism, including the formation of squamous metaplasia, may increase the risk of developing infections and other respiratory diseases (USEPA 1987).

At least some latex paints have been shown to be a source of formaldehyde and acetaldehyde. Since both chemicals have the same irritancy endpoint it is assumed that the levels are additive and that we can use the broader chemical class of total aldehydes when referring to these chemicals.

5.1.3 Solvent Neurotoxicity

Epidemiologic studies on workers have shown neurotoxic effects resulting from both acute and chronic exposures to a variety of solvents, including solvents commonly used in wall paint such as aliphatic and aromatic hydrocarbons, and alcohols. Studies have reported central nervous system (CNS) effects in auto spray painters and shipyard painters. The study on auto spray painters reported that the major solvent components were all below NIOSH REL or OSHA PEL standards, indicating that TVOC levels were probably below 2000 mg/m³. A controlled study of short-term xylene exposures of 90 to 200 ppm found CNS effects.

Acute effects of solvent inhalation include CNS depression, psychomotor impairment, and narcosis. Chronic effects reported in workers are primarily "Type 1" and "Type 2" CNS disorders. Type 1 disorders include fatigue, memory impairment, irritability, difficulty in concentrating, and mild mood disturbance. Type 2 disorders involve mild toxic encephalopathy, including sustained personality or mood changes, and impairment in intellectual function manifested by diminished concentration, memory, and learning capacity. Epidemiologic studies have correlated Type 2 CNS dysfunctions with neurophysiologic parameters such as nerve conduction velocities (NIOSH 1987).

A recent study of workers in two paint manufacturing plants found dose-related effects on olfactory function and on neurobehavioral endpoints. The neurobehavioral effects seen in the study were subclinical in nature and did not give evidence of the more serious neurological effects that have been reported in earlier studies. Historic industrial hygiene monitoring data in both plants allowed the study to include a quantitative exposure analysis. Workers in the lowest exposure quartile had a lifetime-weighted average exposure of about 2 ppm and the highest quartile had a lifetime-weighted average exposure of about

18 ppm. The total exposure concentration represents the sum of the measured concentrations of toluene, xylene, other aliphatic and aromatic hydrocarbons, and methyl ethyl ketone (Bleecker 1991).

5.1.4 TVOC

There are no widely accepted benchmark concentrations that correspond to potential health concerns for Total Volatile Organic Chemical (TVOC) exposures. However, certain studies may provide insight into possible health effects over broad ranges of exposure. An evaluation of field observations made during "sick building syndrome" investigations concluded that headache and other health effects were frequently reported at TVOC levels around 3 mg/m³. Chamber studies with human subjects did not consistently find toxic effects until concentrations reached about 25 mg/m³. One researcher who evaluated a number of chamber and field studies suggested that complaints about indoor air quality (e.g. odor, discomfort) are unlikely to occur at TVOC levels below 0.2 mg/m³, that some complaints may occur at levels between 0.2 mg/m³ and 3 mg/m³ depending on other factors, and that toxic effects are likely to occur at TVOC levels above 25 mg/m³ (Hetes 1992).

5.1.5 C-9 Aromatic Hydrocarbons

Several of the chemicals found in wall paint are C9 aromatic hydrocarbons, i.e., 3- & 4-ethyl toluene, 2-ethyl toluene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene. These chemicals were the subject of a test rule and a RM1 assessment as well. The toxicity tests were conducted on a mixture C9 hydrocarbons. A C9 fraction inhalation developmental toxicity study in mice established a LOEL of 100 ppm. No NOEL was established. Effects on offspring at 100 ppm included an increased frequency of whole litter resorption, increased post-implantation loss, reduced viability and the occurrence of three unusual malformations. A 3-generation C9 fraction inhalation reproductive study in rats showed evidence of parental and reproductive toxicity at all doses, 100, 500 and 1500 mg/kg/day. The LOEL is 100 mg/kg/day. A variety of neurobehavioral effects were observed in the developmental study with mice. The LOEL for neurobehavioral effects was established at 1500 ppm. During the RM1 assessment the following effect levels were established:

LOEL for reproductive toxicity = 100 mg/kg/day
LOEL for developmental toxicity = 210 mg/kg/day

5.1.6 Methyl Ethyl Ketoxime (MEKO)

TSCA §4 testing on methyl ethyl ketoxime (MEKO) was conducted for cancer, chronic toxicity, neurotoxicity, developmental and reproductive toxicity. The hematopoietic system appears to be the primary target of MEKO toxicity. Blood effects have been seen consistently at low doses in all studies that have evaluated that endpoint. No NOAEL for blood effects has been established in studies reviewed to date. The lowest LOAEL for blood effects determined from the available studies is 10 mg/kg/day from the two-generation reproductive toxicity study.

Developmental toxicity was seen in the rabbit study (LOAEL = 24 mg/kg/day; NOAEL = 14 mg/kg/day) but not in either the two-generation rat study (NOAEL = 200 mg/kg/day) or the standard developmental toxicity study in rats (NOAEL = 600 mg/kg/day). These data indicate that the rabbit may be the more sensitive species for this endpoint. EPA staff scientists concluded that because of the uncertainties in interpreting the effects observed in the F0 males in the two-generation reproductive toxicity study, a LOAEL and NOAEL for male reproductive toxicity cannot be defined at present.

MEKO demonstrated carcinogenic activity in long-term inhalation studies, causing liver tumors in both rats and mice. A preliminary quantitative dose response assessment derived a slope factor for the linearized upper bound for extra risk of $1.9 \times 10^{-2} \text{ ppm}^{-1}$. This slope factor is based on the incidence of liver and mammary gland tumors in male rats.

Degeneration of the olfactory epithelium was found at all test concentrations in the chronic inhalation studies in rats and mice. A subchronic inhalation study in mice with 4 and 13-week recovery periods was conducted to further assess the production and reversibility of lesions in the nasopharynx. The NOAEL was 3 ppm (USEPA 1997).

A LOAEL of 300 mg/kg for neurotoxicity and NOAEL of 100 mg/kg were found in a study in which rats received a single oral dose of MEKO. A subchronic oral study in rats found a LOAEL of 400 mg/kg/day for neurotoxicity and a NOAEL of 124 mg/kg/day. All neurologic effects in both studies were transient and were not accompanied by significant neuropathology.

5.1.7 Diethylene Glycol Butyl Ether (2-(2-Butoxyethoxy)ethanol)

The Ethylene Glycol Ethers Toxicology Group of the Chemical Manufacturers Association recently conducted a review of

Diethylene Glycol Butyl Ether (DGBE). This review covers the studies conducted under the TSCA §4 testing program and a number of other unpublished studies as well as the published literature on DGBE. The most relevant study for evaluating inhalation exposures resulting from the use of DGBE in paint appears to be an unpublished 90-day inhalation study rats performed for BASF Corporation in 1992. This study reported a NOAEL of 14 ppm (93 mg/m³) (Gingell et al. 1996).

5.2 Characterization of Exposed Consumer Populations

The characterization of the exposed consumer population was done using data generated by Westat, Inc. in a survey of selected consumer household products (Westat, 1987). Westat surveyed 4,918 people over the age of 18 as to their use of various household products including latex and oil paints. Each survey respondent was asked the same set of questions about both products. The survey contained questions on location, duration and frequency of use, protective measures taken, and user demographics. These data are presented in Table 11. It is assumed for the purpose of this assessment that the oil paint data can be used for alkyd paints, so "alkyd" replaces "oil" in the table.

According to Westat, about 50% of the surveyed persons had ever used latex paint versus about 30% who had used oil paint. By multiplying the number of persons between 18 and 65 as reported in a table dated July 1, 1995 (U.S. Department of Commerce, 1993) with the percent of respondents who had used the paints in the survey, it is estimated that approximately 67 million people have used latex and 28 million people have used alkyd paints indoors in the U.S. (see Table 11). By multiplying the number of persons between 18 and 65 with the percent of respondents who had used the paints in the last year it is estimated that 44 million and 14 million people used latex and alkyd paints indoors, respectively, in 1994.

Table 11 shows that people tend to prefer latex paints over alkyd paints. More people use latex paints, with shorter intervals between uses. The duration of use tends to be longer for latex paints, and more ounces of latex paint are used per year and per event. People tend to use latex paints more often for jobs inside the house (Westat, 1987).

Table 11. Consumer Use Characteristics of Latex and Alkyd Paint Users

Question	Response, Applied to Entire Exposed Population	
	Latex Paint	Alkyd Paint
1. Estimated number of users between 18 and 65: a. All users b. Indoor users (last use)	a. 88,863,247 b. 67,180,614	a. 48,111,092 b. 28,241,211
2. Estimated number of events/year for all users (events/year)	median = 0.57 upper end = 4.5	median = 0.3 upper end = 3.5
3. Estimated number of recent users (within the last twelve months): a. All users b. Indoor users (last use)	a. 58,675,254 b. 44,358,492	a. 24,112,500 b. 14,154,038
4. Duration of use (minutes) for recent users	median = 180 upper end = 480	median = 120 upper end = 480
5. For recent users, number of minutes in the room after the last use (minutes)	median = 5 upper end = 240	median = 0 upper end = 120
6. For recent users, estimated ounces of paint used per year (oz./year)	median = 256 upper end = 858	median = 64 upper end = 384
7. For recent users, estimated number of ounces/use	median = 128 upper end = 448	median = 32 upper end = 256
8. For recent users, location of last use	Basement: 2.8% Living room: 9.9% other inside room: 47.6% several inside rooms: 11.6% garage: 2.0% outside: 24.4% garage and outside: 1.7%	Basement: 5.9% Living room: 5.9% other inside room: 35.4% several inside rooms: 3.3% garage: 6.15% outside: 41.35% garage and outside: 2.1%

9. For recent users, protective measures taken:		
a. opened a door or window to outside	a. 75.8% yes, 24.2% no	a. 69.5% yes, 30.5% no
b. Used an exhaust fan	b. 15.6% yes, 84.4% no	b. 16.4% yes, 83.6% no
c. Opened an inside door to the room	c. 84.7% yes, 15.3% no	c. 68.6% yes, 31.4% no

Source: Westat 1987

To determine the number of events per year for all users, EPA used Westat's empirical cumulative distribution function (ECDF) for the "time since last painting", which is not the same as the "time between painting events." Since it was unclear what the relationship was between the Westat ECDF for the "time since last painting" and the "time between painting events", an additional factor of 2 was applied to the exposure frequency to inflate the inter-event time sampled from the Westat ECDF. This was considered reasonable since on the average it was likely that the respondents were surveyed half way between events.

Subsequently, the number of painting events per year were calculated using the following equation:

$$E_y = 12 / (MLE \times 2) \times PI / 100$$

where E_y = Events per year

MLE = Number of months since the last episode

2 = Correction factor to inflate the inter-event time

PI = Percent of time activity takes place indoors

PI is the percent of indoor use for the last event reported by recent users. This is assumed to equal the percent of time wall paint is used indoors.

The number of indoor paint users is a little more complicated. Many people said their last use of paints had been outside (Westat, 1987). Many users paint part(s) of their homes more than once a year, however, and persons who paint outdoors may logically paint indoors as well. Therefore, the number of indoor users will not simply equal the total number of users minus the persons who last used the paint outdoors. In Table 11, the uncertainty in the number of indoor users is treated by reporting both the total number of users and the number of persons who used paints indoors at the time of the last use.

In Table 11, the term "recent users" refers to survey

participants who had used the product in the last year. Questions 4-6, 8, and 9 were asked only of these people. A distribution for question 7 was derived by Westat based on other answers. Statistics for question 2 were derived by EPA. "Upper end" refers to the ninetieth percentile value as reported by Westat.

5.3 Characterization of Exposed Worker Populations

Wall Paints are applied to residences and offices by do-it-yourself consumers and by professional painters. Typical applications may include homes, apartment complexes, and government or other types of office buildings. Workers typically apply paints by roller or brush (NIOSH, 1980; Kirk-Otthmer, 1993). However, application by airless spray equipment may also be used (NPCA, 1992). Application rates by one painting contractor in the painting of office buildings was estimated to be from one to three gallons per day (NIOSH, 1980).

Paint contractors employ both full-time and temporary personnel (NIOSH, 1980). For full-time employees, exposure durations and working lifetimes are assumed to be up to 250 days/yr and 40 years respectively. For temporary employees the values of these parameters would be somewhat less. The daily exposure duration is assumed to be up to 8 hrs/day. The amount of that time actually spent painting may be somewhat less than that because the painting task will also involve other activities such as mixing, surface preparation and cleanup. However, some exposure could still take place during mixing and cleanup activities.

The number of professional painters potentially exposed to wall paints is estimated to be 146,000. This is based on U.S. Department of Labor Statistics for 1991 for Standard Industrial Classification (SIC) 172. This SIC Code consists of special trade contractors primarily engaged in painting and paper hanging. Included in this classification are house painters and painters of buildings and other structures, the type of painters expected to use wall paints. Because this SIC code includes other types of painters it may overestimate the number exposed to wall paints. However, given the consumption volume of 229 million gallons it is probably a reasonable bounding estimate.

Additionally, information on occupational exposures was obtained by EPA in a phone conversation with Rick Hackney of the International Brotherhood of Painters and Allied Trades (Hackney 1996). Mr. Hackney stated that workers typically spend 250 days per year painting, that 90% of the time workers used latex paint, and that workers about two-thirds of their time was spent painting indoors (Hackney 1996).

5.4 Chemical Concentrations in Air from Paint

It is necessary to know the chemical concentrations in the indoor air in order to estimate exposure of workers and consumers to chemicals emitted by latex and alkyd paint. The most direct method for determining the chemical concentrations is to monitor the indoor air while a room is being painted. Only one study, "Exposure to Volatile Components of Polyvinyl Acetate (PVA) Emulsion Paints During Application and Drying" (ITC 1992 prepared for NPCA), provided exposures to chemicals in paint during typical application conditions. Of all of the chemicals listed as having benchmark hazard data, only three chemicals were measured during this study (formaldehyde, acetaldehyde, and vinyl acetate monomer). Therefore, it was necessary to estimate air concentrations of the other chemicals using small chamber emission data when available. This section will present the monitoring data from the ITC monitoring study as well as describe the method used to estimate indoor air concentrations from small chamber studies.

Latex Paints

Acetaldehyde concentrations in air were taken from the ITC study (ITC 1992). The purpose of this study was to estimate worker and consumer exposure to volatile components of PVA paint during field application. Concentrations in air were measured during application of paint with airless spray equipment and roller/brush combination at 0.5 and 5.0 air exchanges per hour. The study was conducted in unoccupied dorm rooms at a university residence hall (ITC 1992).

In the study, personal breathing zone samples were taken during application of paint. The application phase generally took about twenty to thirty minutes. Six-hour time weighted average (TWA) concentrations were estimated from fixed-station air samples taken during application and drying. Results were presented for six experiments, three airless spray and three

roller/brush. Geometric average concentrations are calculated based on the individual experiment results (ITC 1992).

For the purpose of this RM1 assessment, the geometric average concentrations are used to estimate exposure. Geometric means are not as easily influenced by outliers as are arithmetic means. Exposures were estimated based on the range of the geometric averages of measured concentrations in air. Exposures are calculated based on both personal breathing zone samples and TWAs.

For the purpose of this RM1 assessment, the geometric mean concentrations are used to estimate exposure. Geometric means are not as easily influenced by outliers as are arithmetic means. Exposures were estimated based on the range of the geometric averages of measured concentrations in air. Exposures are calculated based on both personal breathing zone samples and TWAs.

The personal breathing zone samples were taken during the relatively brief time that paint was applied. The TWAs were measured over a six-hour period. Both the personal breathing zone samples and the 6-hour TWAs were used in calculating exposures. In constructing this scenario, it is assumed that personal breathing zone samples and 6-hour TWA concentrations can be applied to the estimated eight-hour exposure duration.

Therefore, exposures calculated based on personal breathing zone samples taken during application involve the assumption that the exposed person is applying paint continuously throughout the 8-hour exposure duration. The use of a 6-hour TWA involves the assumption that the exposed person paints for a few minutes, then is exposed to the drying paint for several additional hours.

The acetaldehyde concentrations in air used in this report, 0.63 parts per million (ppm) and 15.39 ppm, (1.13 mg/m³ and 28 mg/m³), were taken from the ITC report, table I-2, "Summary Statistics for Air Concentrations of Acetaldehyde". These represent the range of geometric average concentrations of acetaldehyde in air (ITC 1992).

Benzaldehyde concentrations in air were taken from the RTI study (RTI 1994). This study provides the results of bulk product analysis and small chamber testing. Both latex and alkyd paints were studied. The concentration in air used in this RM1 assessment, 0.022 mg/m³, is taken from the RTI report, Table 8-35, "Results of Inter-chamber Variability Tests for Aldehyde Emissions from Latex Paint". The RTI table reports results from the use of Sherwin Williams 1604 Gloss (Rose Dawn). Benzaldehyde results for the two tests involved in the use of this paint were

taken at sampling time of 1.3 hours. All other sampling times were greater than the eight-hour exposure duration (RTI 1994).

2-(2-butoxyethoxy ethanol) or diethylene glycol butyl ether (DGBE) concentrations in air were modeled based on chamber concentrations from the "Methodology for Characterizing Indoor Air Emissions from Latex Paint" study (EPA 1995). A model has been developed for estimating emission profiles for chemicals released from interior latex paints, where data are available from small-chamber experiments (Geomet 1997). The emission profile is based on chamber data from "Methodology for Characterizing Indoor Air Emissions from Latex Paint", test 7 (EPA 1995). In this study, SW 99 and RTI latex paints were applied to pre-painted gypsum board, and chemical concentrations in air were measured. These chamber results were used to develop emission parameters and rate constants for the source term equation below. The SW 99 chamber test results were selected for this assessment. These results are similar to the RTI paint concentrations, except that the peak concentrations are higher by about a factor of 3 for the SW 99 paint (EPA 1995).

The source term was represented by a double exponential. The first exponential represents the "fast" emission rate that occurs primarily when the paint is in the wet phase of the drying process. The second exponential represents the "slow" emission rate that occurs during the dry phase (Geomet 1997). The source term equations are presented in Appendix F. Exposure estimation methods are presented in Appendix G.

Formaldehyde concentrations were taken from the ITC study. The concentrations in air used in this report, 0.05 ppm and 0.45 ppm, (0.06 mg/m³ and 0.55 mg/m³), were taken from the ITC report table I-8, "Summary Statistics for Air Concentrations of Formaldehyde" (ITC 1992). These represent the range of geometric average concentrations of formaldehyde in air.

Vinyl acetate concentrations were taken from the ITC study. Vinyl acetate concentrations in air were below the limit of detection in the ITC study. For risk assessment purposes, however, exposures were estimated based on the assumption that the vinyl acetate concentration could be ½ the average limit of detection. The average environmental limit of detection ranged from 0.01 ppm to 0.26 ppm. Therefore, the concentrations in air used in this report are 0.005 ppm and 0.13 ppm, (0.02 mg/m³ and 0.46 mg/m³). These values were taken from the ITC report table I-12, "Summary Statistics for Air Concentrations of Vinyl Acetate" (ITC 1992).

In addition to individual chemical concentrations in air, total **acetaldehyde** and **formaldehyde** concentrations are of interest due to concerns for professional painters for chronic irritation. These concentrations are calculated by summing the individual formaldehyde and acetaldehyde concentrations in air. The results are presented in Table 12. Summary statistics for measured formaldehyde and acetaldehyde concentrations in air are shown in Appendix E (ITC 1992).

Table 12. Acetaldehyde and Formaldehyde Concentrations in Air

Chemical	Concentration in Air (ppm)	
	Lowest Geometric Average Concentration	Highest Geometric Average Concentration
Acetaldehyde	0.63	15.39
Formaldehyde	0.05	0.45
Acetaldehyde + Formaldehyde	0.68	15.84
Chronic Irritation Benchmark	0.1 ppm	

Source: ITC 1992

Alkyd Paints

C9 Aromatic Hydrocarbon concentrations were taken from the RTI report, table 8-16, "Results of Single Chamber Repeatability Tests (Tests 5 and 6) For VOC Emissions From Alkyd Paints - Chamber Air Concentration". The concentration in air used in this report, 138.8 mg/m³ was taken from tests 5 and 6. This concentration is the average value from both tests, averaged over the first 7.8 hours. The tests were performed on Glidden 4550-76262 Gloss (Hyacinth).

Xylene concentrations were taken from the RTI study, table 8-16, "Results of Single Chamber Repeatability Tests (Tests 5 and 6) For VOC Emissions From Alkyd Paints - Chamber Air Concentration". The concentrations in air used in this report, 64.6 mg/m³ for m,p-xylene and 22.7 mg/m³ for o-xylene, were taken from tests 5 and 6. These concentrations are the average values for each chemical, averaged over the first 7.8 hours. The tests were performed on Glidden 455-76262 Gloss (Hyacinth).

Methyl Ethyl Ketoxime (MEKO) concentrations are discussed elsewhere in the dossier. Exposures were calculated based on concentrations in air from the test rule for methyl ethyl ketoxime. No new information was available when this assessment was completed. Therefore, the estimated exposures from the test rule have been retained.

5.5 Exposure Estimation for Workers and Consumers

Four exposure equations are presented in this RM1 assessment. The choice of the appropriate exposure value depends on the hazard benchmark available for a given chemical, and its units. The exposure calculations presented in this report are Average Daily Concentrations (ADCs), Average Daily Doses (ADDs), Lifetime Average Daily Concentrations (LADCs), and Acute Potential Dose Rates (APDRs).

Central tendency exposures are estimated in this RM1 assessment. Central tendency is a type of exposure descriptor. These descriptors indicate where the estimated exposure falls on the expected distribution of actual exposures received by workers and consumers. Central tendency estimates present the estimated mean or median value for the exposed population (EPA 1992).

Equations

The Average Daily Concentration (ADC) calculation is as follows:

$$\text{ADC (mg/m}^3\text{)} = (\text{Conc} \times \text{HRS} \times \text{EV} \times \text{FQ} \times \text{UL}) / 24 \times \text{UL} \times 365$$

where

Conc = Time-weighted average concentration in air (mg/m³)
Hrs = Hours of exposure per day (hours/event)
EV = Number of events per day (event/day)
FQ = Frequency of events per year (days/year)
UL = Years of exposure per lifetime (years)
24 = Total hours per day (hours/day)
365 = Days per year (days/year)

The Average Daily Dose (ADD) Equation is as follows:

$$\text{ADD (mg/kg/day)} = (\text{Conc} \times \text{HRS} \times \text{EV} \times \text{FQ} \times \text{UL} \times \text{IR}) / \text{BW} \times \text{UL} \times 365$$

where

IR = Inhalation Rate (m³/hr)
BW = Body weight (kg)

The Lifetime Average Daily Concentration (LADC) is as follows:

$$\text{LADC (mg/m}^3\text{)} = (\text{Conc} \times \text{HRS} \times \text{EV} \times \text{FQ} \times \text{UL}) / 24 \times \text{LT} \times 365$$

where LT is the number of years per lifetime

The Acute Potential Dose Rate equation is as follows:

$$\text{APDR (mg/kg/day)} = (\text{Conc} \times \text{HRS} \times \text{EV} \times \text{IR}) / \text{BW}$$

Default Values

Default values for the preceding equations are as follows:

Conc:	Chemical-specific
Hrs:	8 hours/event for both workers and consumers
EV:	1 event/day for both workers and consumers
IR:	1.25 m ³ /hr inhaled by both workers and consumers (EPA 1989)
BW:	72 kilograms for both workers and consumers (EPA 1989)
FQ:	0.57 days/year - consumer use of latex paint i.e., used approximately once every two years (Westat 1987) 0.3 days/year - consumer use of alkyd paint i.e., used approximately once every three years (Westat 1987) 141 days/year - worker use of latex paint (Assumes latex paints are used 90% of the time) (Hackney 1996) 16 days/year - worker use of alkyd paint (Assumes alkyd paints are used 10% of the time) (Hackney 1996)
UL:	47 years of use per lifetime for consumers (Westat 1987)

40 years of use per lifetime for workers (standard EPA assumption)

LT: 75 years per lifetime for both workers and consumers (EPA 1989)

Table 13 and 14 shows chemical concentrations and the associated exposures in latex paint and alkyd paint, respectively.

Table 13. Estimated Exposures for Latex Paints

Chemical	Conc. in Air (mg/m ³)	Estimated Exposure	Exposed Population	Exposure Type
Acetaldehyde	1.13-28	0.2-4 mg/m ³	worker	ADC
		0.0006-0.01 mg/m ³	consumer	ADC
		0.08-2 mg/m ³	worker	LADC
		0.0004-0.009 mg/m ³	consumer	LADC
Benzaldehyde	0.022	0.001 mg/kg/day	worker	ADD
		0.000005 mg/kg/day	consumer	ADD
DGBE	2.87	0.37 mg/m ³	worker	ADC
		0.001 mg/m ³	consumer	ADC
Formaldehyde	0.06-0.55	0.003-0.03 mg/kg/day	worker	ADD
		0.00001-0.0001 mg/kg/day	consumer	ADD
		0.004-0.04 mg/m ³	worker	LADC
		0.00002-0.0002 mg/m ³	consumer	LADC
Vinyl Acetate	0.02-0.46	0.003-0.06 mg/m ³	worker	ADC
		0.00001-0.0002 mg/m ³	consumer	ADC
		0.001-0.02 mg/kg/day	worker	ADD
		0.000004-0.0001 mg/kg/day	consumer	ADD

Table 14. Estimated Exposures for Alkyd Paints

Chemical	Conc. in Air (mg/m ³)	Estimated Exposure	Exposed Population	Exposure Type
C9 Aromatic Hydrocarbons	138.8	0.8 mg/m ³	worker	ADD
		0.02 mg/m ³	consumer	ADD
		19	worker	APDR
		19	consumer	APDR
m,p-xylene	64.6	0.4 mg/kg/day	worker	ADD
		0.007 mg/kg/day	consumer	ADD
o-xylene	22.7	0.1 mg/kg/day	worker	ADD
		0.003 mg/kg/day	consumer	ADD

6.0 RISK ASSESSMENT

6.1 Quantitative Risk Estimates

The type risks estimated in this assessment depends on the available hazard benchmark(s) for each chemical. Hazard quotients (HQs) and Cancer risks are estimated for latex paint. Margin of Exposure (MOE) for developmental and reproductive effects and Hazard Quotients are estimated for alkyd paint. Tables 15 and 16 lists the hazard benchmark value and risks for chemicals in latex and alkyd paints. The equations for estimating risk are shown below. All risks are unitless.

Hazard Quotient = $\text{ADC}(\text{mg}/\text{m}^3) / \text{Inhalation Reference Concentration}(\text{RfC}) (\text{mg}/\text{m}^3)$

Or = $\text{ADD} (\text{mg}/\text{kg}/\text{day}) / \text{Oral Reference Dose} (\text{RfD}) (\text{mg}/\text{kg}/\text{day})$

Cancer risk = $\text{LADC} (\text{mg}/\text{m}^3) \times \text{Unit Risk} (\text{mg}/\text{m}^3)^{-1}$

MOE = $\text{Lowest Observed Effect Level} (\text{LOEL}) (\text{mg}/\text{kg}/\text{day}) / \text{ADD} (\text{mg}/\text{kg}/\text{day})$

Or = $\text{No Observed Adverse Effect Level} (\text{NOAEL}) (\text{mg}/\text{kg}/\text{day}) / \text{ADD} (\text{mg}/\text{kg}/\text{day})$

Table 15. Estimated Risks for Chemicals in Latex Paints

Chemical Name	Type of Risk Estimated	Occupational Value	Consumer Value
Acetaldehyde	Hazard Quotient (unitless)	22-440	0.07-1
Acetaldehyde	Cancer Risk (unitless)	2E-4 - 4E-3	1E-6 - 2E-5
Benzaldehyde	Hazard Quotient	0.001	0.000005
2-(2-butoxyethoxy) ethanol (or DGBE)	Margin of exposure	250	93000

Formaldehyde	Hazard Quotient	0.002 - 0.02	5E-6 - 5E-5
Formaldehyde	Cancer Risk Unit Risk from IRIS = 0.013 (mg/m ³) ⁻¹	5E-5 - 5E-4	3E-7 - 3E-6
Formaldehyde	Cancer Risk Unit Risk from PBPK#1 = 0.0022 (mg/m ³) ⁻¹	9E-6 - 9E-5	4E-8 - 4E-7
Formaldehyde	Cancer Risk Unit Risk from PBPK #2 = 0.00026 (mg/m ³) ⁻¹	1E-6 - 1E-5	5E-9 - 5E-8
Vinyl Acetate	Hazard Quotient	0.02 - 0.3	5E-4 - 1E-3
Vinyl Acetate	Hazard Quotient	0.001 - 0.02	4E-6 - 1E-4

Table 16. Estimated Risks for Chemicals in Alkyd Paints

Chemical Name	Variable Name (units)	Occupational Value	Consumer Value
C9 aromatic hydrocarbons: 2-ethyl toluene 3-ethyl toluene and 4-ethyl toluene 1,2,3-trimethylbenzene 1,2,4-trimethylbenzene 1,3,5-trimethylbenzene	Margin Of Exposure (MOE _{LOAEL}) for reproductive effects (unitless)	125	5000
C9 aromatic hydrocarbons	MOE _{LOAEL} for developmental effects	11	11
Methyl Ethyl Ketoxime	MOE _{NOAEL} for developmental tox	3.0	3.0
	MOE _{LOAEL} for blood effects	3.1	220
	Cancer risk (slope factor from \$4 study)	3.5E-2	8.5E-4
m,p-xylene	Hazard Quotient	0.2	0.004

o-xylene	Hazard Quotient	0.05	0.002
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6.2 Risk Conclusions

6.2.1 Alkyd paints

- MOE estimates indicate a concern for developmental and reproductive risks from C9 aromatic hydrocarbons for both consumers and professional painters.
- A concern exists for acute CNS effects from total solvent exposure in both consumers and professional painters. Approximate 8-hr TWA TVOC levels exceeded 2000 mg/m³ for all samples under all conditions. Xylene concentrations from some samples approached the levels at which neurologic effect were seen in one short-term study.
- High solvent exposures as indicated by TVOC measurements also indicate a concern for chronic CNS effects in professional painters.
- TVOC levels indicate a high likelihood of complaints about indoor air quality during and shortly after painting.
- For methyl ethyl ketoxime, the MOE_{NOAEL} for developmental toxicity for both consumers and professional painters is about 3.0, indicating a clear concern for this effect. The MOE_{LOAEL} for blood effects (the most sensitive chronic effect) is about 220 for consumers, indicating a possible concern for this effect and 3.1 for professional painters, indicating a clear concern. Cancer risk estimates based on a preliminary slope factor derived from the S4 inhalation study indicate a concern for both consumers and professional painters.

6.2.2 Latex paints

- Hazard quotient estimates indicate a concern for chronic risks from acetaldehyde for professional painters. Acetaldehyde also presents a possible concern for cancer risk to professional painters, with risk estimates around 10⁻⁴ based on currently available potency estimates. It is a B2 carcinogen with uncertainties about its actual carcinogenic mechanism. It appears to be an initiator, albeit a weak one, based on the high levels needed to induce

cancers. If acetaldehyde's mechanism of carcinogenicity is similar to that of formaldehyde, the carcinogenic potency of acetaldehyde at low concentrations is probably significantly lower than the current potency estimates that were calculated by the standard linear extrapolation. Respiratory exposure is anticipated to be the route of greatest concern.

- Formaldehyde presents a marginal concern for cancer risk to professional painters. Risk estimates based on the unit risk value derived from the traditional linear extrapolation of tested air concentrations are around 10^{-4} . However, EPA has developed alternative unit risk values for low-level exposures (below 1 ppm) based on internal dosimetry in rats and monkeys (Hernandez 1994). Because the average concentrations of formaldehyde encountered by painters are expected to be well below 1 ppm, the dosimetric models appear to be relevant to the scenario. Risk estimates using unit risk values from the dosimetric models are in the 10^{-5} to 10^{-6} range.
- Formaldehyde presents concern for acute irritation for both consumers and professional painters. There is a concern for irritation based on concentrations of formaldehyde in the room during painting and at 6 hours after painting. The concentrations are generally greater than the 0.1 ppm level at which some people experience eye irritation. There is also a concern for chronic irritation in professional painters since formaldehyde concentrations are often in the range at which chronic effects (mucociliary inhibition, squamous metaplasia) have been observed. It is expected that there would be irritation effects for other aldehydes, including acetaldehyde.
- TVOC levels are in the range that may result in complaints about indoor air quality. All samples and test conditions in the chamber studies resulted in TVOC levels exceeding 40 mg/m^3 as an approximate 24-hr TWA.
- At least some latex paint has been shown to be a source of formaldehyde and acetaldehyde. The exact concentrations of these chemicals or the exact reason these chemicals are emitted from latex paint has not been well characterized. It has been shown that concentrations are in the range of concern for irritancy. This can be a problem for workers who are exposed every day to fresh paint and less of a concern for consumers since the emissions may drop below levels of concern relatively rapidly. Since both formaldehyde and acetaldehyde have the same irritancy

endpoint, it is assumed that the levels are additive and the broader chemical class of "total aldehydes" is used when referring to these chemicals. The lower the amount of the total aldehydes that are emitted from paint the better since these chemicals are irritating to the eyes and respiratory system. The action level commonly used for formaldehyde from pressed wood products is 0.1 ppm (part per million in air).

7.0 CONCLUSIONS

It is recognized that the paint industry is in the state of flux with regards to lowering the VOC¹ content of paint mainly due to existing or impending regulations whose goal is to reduce ground-level ozone. Indeed the market place has already made a major switch from solvent-based to water-based paint in the last 20 years. There is evidence that the industry is aware of indoor air issues by the fact that some companies have developed and marketed "no-VOC" latex paints that have less odor.

Additionally, the National Paint and Coatings Association has been participating in EPA's Designing Wall Paint for the Indoor Environment project. The goal of the Wall Paint DfE project is to provide industry with a tool kit that they can use to estimate exposure/risk to chemicals formulated into paint during the design phase or as a product stewardship effort.

Although industry has made significant improvements, EPA feels that the analysis presented in this document sketches out concerns that should be addressed. Specific recommendations made at a Office and Division Directors meeting held on September 24, 1996 were: that the RM1 phase would be completed with the revision of this report, that latex paint would be dropped from further RM review, and that certain chemicals in alkyd paints

would be reviewed under other OPPT programs. The reason for this action is that, although fewer people are exposed to alkyd paint than latex paint, there is still a significant population (an estimated 14 million consumers) exposed. Professional painters (an estimated 147 thousand) will be exposed also. Some alkyd paint constituents, C9 aromatic hydrocarbons and methyl ethyl ketoxime, have been shown to be developmental toxicants in animal studies. The C9s have been shown to have reproductive effects in animal studies.

The concern for developmental effects is especially troubling because exposure to developmental toxicants need only occur on one day (when the fetus is susceptible) for the effect to occur. Exposure data is being generated by EPA's Office of Research and Development on several alkyd paint formulations.

¹Footnote: It is important to note that the term "VOC" has a specific definition under the Clean Air Act that does not correspond to the term TVOC used in the indoor air arena. Chemicals that are excluded from the VOC definition are not excluded when discussing indoor air TVOC. TVOCs are defined by the analytical methods used to test products (usually in small/large chambers). Currently, however, there is not a uniform definition for TVOC.

Additionally, it is anticipated that exposure testing is to be done by MEKO manufacturers of exposures during paint episodes where alkyd paint containing MEKO is being used. This exposure data and/or other information and a subsequent risk assessment are needed to evaluate alkyd paints.

Since the issues identified in RM1 concerns consumer or worker exposure, CPSC, OSHA, and NIOSH have been briefed on the conclusions of the RM1 analysis and are interested in EPA's current activities as observers. The General Services Administration (GSA) has selected latex paint to develop attributes for environmental preferability. Total aldehydes has been proposed as an environmental attribute for latex paint in the GSA project. ITC test data on one latex paint showed formaldehyde and acetaldehyde concentrations above the 0.1 ppm level at which some people experience eye irritation. It is not known whether this level is common in all painting episodes or whether these levels shown were an anomaly. It is suspected that the formaldehyde present in latex paint is a contaminant or decomposition product of a biocide.

8.0 REFERENCES

Bleecker, M. et al 1991. Dose-Related Subclinical Neurobehavioral Effects of Chronic Exposure to Low Levels of Organic Solvents. Amer J Ind Med 19:715-728.

Chang, John. 1996. Personal Communication between J. Chang, Research Triangle Park, and Christina Cinalli, Office of Pollution Prevention and Toxics, 1996.

Chemical Marketing Reporter. 1994. Cargill Sees Linseed Use As Solvent Replacement, May 2, 1994.

Dang, Winston. 1995. Internal communication between W. Dang Office of Pesticide Programs and Christina Cinalli, Office of Pollution Prevention and Toxics, March 1995.

EPA. 1987. Assessment of Health Risks to Garment Workers and Certain Home Residents from Exposure to Formaldehyde. U. S. Environmental Protection Agency, Office of Pesticides and Toxic Substances, Washington, DC.

EPA. 1989a. Exposure Factors Handbook. Exposure Assessment Group, Office of Health and Environmental Assessment, Environmental Protection Agency.

EPA. 1992b. Interior Architectural Coatings Market Study. Office of Pollution Prevention and Toxics, Regulatory Impacts Branch. September 30, 1992.

EPA. 1992. US Environmental Protection Agency. Guidance on Risk Characterization for Risk Managers and Risk Assessors. May, 1992.

EPA. 1993. Chemical Use Clusters Scoring Methodology, Draft Report. U.S. Environmental Protection Agency, Office Pollution Prevention and Toxics, Regulatory, Chemical Engineering Branch, Washington, DC. July 23, 1993.

EPA. 1995. Methodology for Characterizing Indoor Air Emissions from Latex Paint. Indoor Air Branch, Air Pollution Prevention and Control Division, National Risk Management Research Laboratory, Research Triangle Park, NC.

Geomet. 1997. Estimation of Emission Profiles for Latex and Alkyd Paints. Prepared for the Office of Pollution Prevention and Toxics, Environmental Protection Agency.

Gingell et al. 1996. Toxicology of Diethylene Glycol Butyl Ether. *Occupational Hygiene*, Vol. 2, pp. 293-302.

GEOMET. 1997. Source Ranking Database, Volume 1: Guide and Documentation. Prepared for the Office of Pollution Prevention and Toxics, Environmental Protection Agency.

Hackney, Rick. 1996. Personal communication between R. Hackney, International Brotherhood of Painters and Allied Trades, and Mary Katherine Powers, Office of Pollution Prevention and Toxics, March 1996.

Hetes, R. et al. 1992. Evaluation of Health-Based TVOC Exposures Related to Carpet Emissions. Research Triangle Institute. Research Triangle Park, NC. Report prepared for Carpet and Rug Institute, Dalton, GA.

Hernandez, O. et al. 1994. Risk assessment of formaldehyde. *J Hazardous Materials* 39: 161-172.

Klein, R.J. 1993. Formulating Low-Odor, Low-VOC Interior Paints. *Modern Paint and Coatings*. March, 1993.

Koontz, Michael. 1996. Personal Communication between M. Koontz, Geomet, and Mary Katherine Powers, Office of Pollution Prevention and Toxics, October 1996.

NPCA. 1992. Exposure to Volatile Components of Polyvinyl Acetate (PVA) Emulsion Paints During Application and Drying. Prepared by International Technology Corporation for the National Paint and Coatings Association. February 1992.

NPCA. 1992. U.S. Paint Industry Database. National Paint and Coatings Association.

Modern Paint and Coatings. 1993. Make it Solvent-Free. Keep the Properties You Want with Vinamul 3692. (Advertising supplement) September, 1993.

Mullin, R. 1994. Paints & Coatings. *Chemical Week*. October 12, 1994.

NIOSH 1987. Current Intelligence Bulletin 48. Organic Solvent Neurotoxicity. National Institute for Occupational Safety and Health, Cincinnati, OH. DHHS pub. no. 87-104.

Rauch Associates, Inc. 1990. The Rauch Guide to the U.S. Paint Industry. Co.

Reisch, M.S. 1994. Paints & Coatings. Chemical & Engineering News. October 3, 1994.

Reisch, M.S. 1994. Paints & Coatings. Chemical & Engineering News. October 18, 1993.

RTI. 1994. Revised Final Report, Determination of Test Methods for Interior Architectural Coatings. Prepared for the Environmental Protection Agency. May 1994.

Rohm & Haas Resin Review. 1992. Two Binders for Solvent-Free Indoor Paint. (Advertising supplement) Vol. XLII, No.2.

USEPA 1997. RM1 Risk Assessment of Methyl Ethyl Ketoxime. Office of Pollution Prevention and Toxics. US Environmental Protection Agency. Washington, DC. April 22, 1997.

U.S. Department of Commerce. 1993. 1993 Current Population Report P25-1104: Population Projections of the U.S. by Age, Sex, Race, and Hispanic Origin, 1993-2050. U.S. Department of Commerce, Bureau of the Census.

Ulyatt, J. 1993. Solvent and Odour-Free Paints for Indoor Use. Paint & Ink International. September 1993.

Weismantel, G.E. 1981. Paint Handbook. McGraw-Hill Book Co., New York.

Westat. 1987. 1987 Household Solvent Products: A National Usage Survey. Westat, Inc. for US EPA/OPPT under Contract No. 68-02-4243.

Appendix A. Biocides Listed in OPP Database As Revised by Troy Corp.

03/09/95

REFERENCE FILES SYSTEM
CHEMICALS FOR SITE

PAGE 1 OF 2

81009 -PAINTS (LATEX) (IN-CAN PRESERVATION) (PRESERVATIVE INCORP)

PC CODE CHEMICAL NAME

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4202 Dehydroabietylamine pentachlorophenate
8707 2-Bromo-4'-hydroxyacetophenone
9802 Benzyl alcohol
11101 Barium metaborate
11102 Borax (B4Na2O7.10H2O) (1303-96-4)
14703 Sodium hypochlorite
17901 1-(3-Chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride
17902 (Z)-1-(3-Chloro-2-propenyl)- 3,5,7-triaza-1-azoniatricyclo
      (3.3.1.1 (superscript3,7))decane, chloride
22501 Copper (metallic)
24002 Copper 8-quinolinolate
27901 3,4,4'-Trichlorocarbanilide
34803 Potassium dimethyldithiocarbamate
34805 Zinc dimethyldithiocarbamate
35601 Bis (trichloromethyl) sulfone
35602 Tetrahydro-3,5-dimethyl-2H-1,3,5- thiadiazine-2-thione
35603 2-(Thiocyanomethylthio) benzothiazole
35604 S-(2-Hydroxypropyl) thiomethanesulfonate
43001 Formaldehyde
43901 Glutaraldehyde
44901 2,2' Methylenebis(3,4,6 trichlorophenol)
51705 2-Mercaptobenzothiazole, zinc salt
60101 2-(4' Thiazolyl)benzimidazole
63001 Pentachlorophenol
63003 Pentachlorophenol, sodium salt
64001 Phenol
64002 Sodium phenate
64103 o-Phenylphenol
64104 Sodium o-phenylphenate
66003 Phenylmercuric acetate
66022 Phenylmercuric oleate
68102 Methylenebis(thiocyanate)
68901 2,3,5,6-Tetrachloro-4-(methylsulfonyl)pyridine
69107 Alkyl* dimethyl benzyl ammonium chloride *(100% C14)
69141 Alkyl* dimethyl ethylbenzyl ammonium cyclohexylsulfamate
      *(50%C12, 30%C14, 17%C16, 3%C18)
69141 Alkyl* dimethyl benzyl ammonium chloride *(58%C14,28%C16, 14FC12)
69152 Alkyl* amine hydrochloride *(as in fatty acids of coconut oil)
72501 Silver
77402 4',5-Dibromosalicylanilide
77404 3,4',5-Tribromosalicylanilide
77405 3,5-Dibromosalicylanilide
81301 cis-N-Trichloromethylthio-4-cyclohexene-1,2-dicarboximide
  
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Appendix A. Biocides Listed in OPP Database As Revised by Troy Corp. (Continued)

03/09/95

REFERENCE FILES SYSTEM
CHEMICALS FOR SITE

PAGE 2 OF 2

81009 -PAINTS (LATEX) (IN-CAN PRESERVATION) (PRESERVATIVE INCORP)

PC CODE CHEMICAL NAME

81601	N-((Trichloromethyl)thio)phthal imide
81901	Tetrachloroisophthalonitrile
82901	1,3,5-Triethylhexahydro-s-triazine
82302	Tripolytin methacrylate
83301	Hexahydro-1,3,S-tris(2-hydroxyethyl)-s-triazine
83902	2-(Hydroxymethyl)-2-nitro-1,3-propanediol
86801	4-Chloro-3,S-xyleneol
88002	Zinc 2-pyridinethiol-1-oxide
88004	1-Hydroxy-2-(1H)-pyridinethione, sodium salt
98901	1,2-Benzisothiazolin-3-one
99001	2-((Hydroxymethyl)amino)ethanol
100801	4-(2-Nitrobutyl)morpholine
100802	4,4'-(2-Ethyl-2-nitrotrimethylene)dimorpholine
101001	Diiodomethyl p-chlorophenyl sulfone
101002	Diiodomethyl p-tolyl sulfone
101801	2,2-Dibromo-3-nitrilopropionamide
102901	Potassium N-hydroxymethyl-N-methyldithiocarbamate
104001	2-((Hydroxymethyl)amino)-2-methyl-1-propanol
106801	1,1'-(2-Butenylene)bis(3,5,7-triaza-1-azoniaadamantane chloride)
107001	5-Hydroxymethoxymethyl-1-aza-3,7-dioxabicyclo(3.3.0) octane
107002	5-Hydroxymethyl-1-aza-3,7-dioxabicyclo(3.3.0)octane
107003	5-Hydroxypoly(methyleneoxy)*methyl-1-aza-3,7-dioxabicyclo (3.3.0)octane *(74% C2, 21% C3, 4% C4, 1% C5)
107103	5-Chloro-2-methyl-3(2H)-isothiazolone
107104	2-Methyl-3(2H)-isothiazolone
107801	3-Iodo-2-propynyl butylcarbamate
111001	1-Bromo-1-(bromomethyl)-1,3-propanedicarbonitrile
111286	Phosphoric acid, mono(2-ethylhexyl) ester
114801	4,4-Dimethyloxazolidine
114802	3,4,4-Trimethyloxazolidine
115501	1,3-Dimethylol-5,5-dimethylhydantoin
115502	Monomethylol-5,5-dimethylhydantoin
123702	Methanol, (((2-(dihydro-5-methyl-3(2H)-oxazolyl)-1-methyl)ethoxy)methoxy)methoxy-
128859	Zinc borate (3ZnO, 2B03, 3.5H2O, mw 434.66)
128889	3,5,7-Triaza-1-azoniatricyclo(3.3.1.1(superscript3,7)) decane,1-methyl-, chloride
128996	N-Cyclopropyl-N'-(1E1-dimethylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine
129015	Zinc
129079	Phosphoric acid, bis(2-ethylhexyl) ester, compd. with 2,2'-(cocoalkylimino)bis(ethanol)
129080	Phosphoric acid, mono(2-ethylhexyl) ester,

216400 compds. with diethanolamine N-coco alkyl derivs. (1:1)
2-Bromo-2-nitropropane-1,3-diol

Appendix A. Biocides Listed in OPP Database As Revised by Troy Corp. (Continued)

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REFERENCE FILES SYSTEM
CHEMICALS FOR SITE

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81019: PAINTS (LATEX) (PRESERVATION OF APPLIED FILMS)
(PRESERVATIVE INCORP) PC CODE CHEMICAL NAME

PC CODE	CHEMICAL NAME
6308	5-Hydroxytetracycline monohydrochloride
11101	Barium metaborate
11102	Borax (B ₄ Na ₂ O ₇ ·10H ₂ O) (1303-96-4)
11701	trans-1,2-Bis(propylsulfonyl)ethylene
22501	Copper (metallic)
24002	Copper 8-quinolinolate
34805	Zinc dimethyldithiocarbamate
35505	3-(3,4-Dichlorophenyl)-1,1-dimethylurea
35603	2-(Thiocyanomethylthio)benzothiazole
35604	S-(2-Hydroxypropyl) thiomethanesulfonate
51705	2-Mercaptobenzothiazole, zinc salt
60101	2-(4'-Thiazolyl)benzimidazole
60102	2-(4-Thiazolyl)benzimidazole, hypophosphite salt
63001	Pentachlorophenol
63003	Pentachlorophenol, sodium salt
63004	Tetrachlorophenols
64001	Phenol
64002	Sodium phenate
66003	Phenylmercuric acetate
66022	Phenylmercuric oleate
68901	2,3,5,6-Tetrachloro-4-(methylsulfonyl)pyridine
69135	Alkyl* dimethyl ethylbenzyl ammoniumcyclohexylsulfamate *(50%C12, 30%C14, 17%C16, 3%C18)
72501	Silver
81601	N-((Trichloromethyl)thio)phthalimide
81901	Tetrachloroisophthalonitrile
83001	Bis(tributyltin) oxide
83102	Bis(tributyltin) salicylate
83112	Tributyltin fluoride
83202	Tripropyltin methacrylate
86801	4-Chloro-3,5-xyleneol
99001	2-((Hydroxymethyl)amino)ethanol
99901	2-Octyl-3(2H)-isothiazolone
101001	Diiodomethyl p-chlorophenyl sulfone
101002	Diiodomethyl p-tolyl sulfone
107001	5-Hydroxymethoxymethyl-1-aza-3,7-dioxabicyclo(3.3.0)octane
107002	5-Hydroxymethyl-1-aza-3,7-dioxabicyclo(3.3.0)octane
107003	5-Hydroxypoly(methyleneoxy)*methyl-1-aza-3,7-dioxabicyclo (3.3.0)octane *(74% C2, 21% C3, 4% C4, 1% C5)
107801	3-Iodo-2-propynyl butylcarbamate
111001	1-Bromo-1-(bromomethyl)-1,3-propanedicarbonitrile
111286	Phosphoric acid, mono(2-ethylhexyl) ester
128909	7a-Ethyldihydro-1H,3H,5H-oxazolo(3,4-c)oxazole
128996	N-Cyclopropyl-N'-(1,1-dimethylethyl)-6-(methylthio)- 1,3,5-triazine-2,4-diamine
129015	Zinc
129079	Phosphoric acid, bis(2-ethylhexyl) ester, compd. with 2,2'-(cocoalkylimino)bis(ethanol)
129080	Phosphoric acid, mono(2-ethylhexyl) ester, compds. with

~~diethanolamine-N-coco-alkyl derivs. (1:1)~~

Appendix A. Biocides Listed in OPP Database As Revised by Troy Corp. (Continued)

03/09/95

REFERENCE FILES SYSTEM

PAGE 1 OF 1

CHEMICALS FOR SITE

97003: PAINT FILMS AND THE SURFACES THEY COVER

PC CODE CHEMICAL NAME

~~21302~~ ~~Copper naphthenate~~
24002 Copper 8-quinolinolate
60101 2 - (4' -Thiazolyl)benzimidazole
~~66022~~ ~~Phenylmercuric oleate~~
81901 Tetrachloroisophthalonitrile
83001 Bis(tributyltin) oxide

Appendix B. Wall Paint chemicals by paint type and function							
Casno	Chemical Name	PAINT TYPE		FUNCTION OF CHEMICAL			
		L a t e x	A l k y d	Solvent /Inter- mediate	Pigment	Resin/ Inter- mediate	Additive
75-07-0	Acetaldehyde	x		x			
107-13-1	Acrylonitrile	x				x	
*****	Aluminum silicate	x			x		
1336-21-6	Ammonium hydroxide	x					x
7440-36-0	Antimony Compound	x			x		
	Benzyl bromoacetate	x					x
106-99-0	Butadiene	x				x	
112-34-5	2-(2-Butoxyethoxy)ethanol	x		x			
124-17-4	2-(2-Butoxyethoxy) ethyl acetate	x		x			
141-32-2	Butyl acrylate	x				x	
141-96-1	n-Butyl ether	x		x			
1317-65-3	Calcium carbonate	x	x		x		
1333-86-4	Carbon black	x	*		x		
9004-30-2	Carboxymethyl hydroxyethyl cellulose	x					x
4080-31-3	1-(3-Chloroallyl)-3,5,7-triaza-1-azoniaadamantane	x					x
1332-58-7	Kaolin	x	*		x		
61789-51-3	Cobalt napthenate		x				x
13586-82-8	Cobalt 2-ethylhexanoate		x				x
7440-47-3	Chromium compounds		x		x		
91-17-8	trans-Decahydronaphthalene		x	x			
11-46-6	Diethylene Glycol	x		x			
24806-32-4	Di(phenylmercuric) dodecyl succinate	x					x
26761-40-0	Diisodecyl phthalate	x					x
103-23-1	Diocetyl adipate	x					x
117-81-7	Diocetyl phthalate	x					x

Appendix B. Wall Paint chemicals by paint type and function

Casno	Chemical Name	PAINT TYPE		FUNCTION OF CHEMICAL			
		L a t e x	A l k y d	Solvent /Inter- mediate	Pigment	Resin/ Inter- mediate	Additive
110-98-5	Dipropylene glycol	x				x	
124-18-5	n-Decane		x	x			
112-40-3	n-Dodecane		x	x			
84-74-2	Dibutylphthalate	x					x
121-69-7	Dimethyl aminoazobenzene		x	x			
140-88-5	Ethyl acrylate	x				x	
100-41-4	Ethyl benzene	x				x	
107-21-1	Ethylene glycol	x		x			
103-11-7	2-Ethylhexyl acrylate	x				x	
611-14-3	2-Ethyl toluene		x	x			
622-96-8	Ethyl toluene(3&4)		x	x			
50-00-0	Formaldehyde	x				x	
107-41-5	Hexylene glycol	x		x			
9004-62-0	Hydroxyethyl cellulose	x					x
9004-65-3	Hydroxypropyl methyl cellulose	x					x
****	Iron oxide	x	*		x		
121-91-5	Isophthalic acid		x			x	
7439-92-1	Lead compounds		x				x
68910-52-1	Lecithin(soybean)	x					x
1336-93-2	Manganese napthenate		x				x
676-56-1	Methanol		x	x			
71-55-6	Methyl chloroform(1,1,1-Trichloroethane)		x	x			
6975-98-0	2-Methyldecane		x	x			
78-93-3	Methyl ethyl ketone(2-butanone)		x	x			
96-29-7	Methyl ethyl ketoxime		x				x

Appendix B. Wall Paint chemicals by paint type and function

Casno	Chemical Name	PAINT TYPE		FUNCTION OF CHEMICAL			
		L a t e x	A l k y d	Solvent /Inter- mediate	Pigment	Resin/ Inter- mediate	Additive
108-10-1	Methyl isobutyl ketone (hexone)		x	x			
80-62-6	Methyl methacrylate	x				x	
75-65-0	2-methyl-2-propanol	x		x			
67-68-5	methyl sulfoxide	x		x			
7440-2-0	nickel Compounds	x					x
111-84-2	n-Nonane		x	x			
NA	Polyhydric alcohol		x			x	
9003-20-7	Polyvinyl acetate	x				x	
13845-36-8	Potassium tripolyphosphate	x					x
103-65-1	n-propyl benzene	x		x			
61203-99-4	Propylcyclohexane		x	x			
57-55-6	Propylene Glycol	x		x			
4292-92-6	Pentylcyclohexane		x	x			
62-38-4	Phenylmercuric acetate	x					x
104-60-9	Phenylmercuric oleate	x					x
85-44-9	Phthalic anhydride		x			x	
7631-86-9	Silica	x	*		x		
1639-66-3	Sodium dioctyl sulfosuccinate	x					x
54193-36-1	Sodium polymethacrylate	x					x
100-42-5	Styrene	x	x			x	
14807-96-6	Talc	x	*		x		
25265-77-4	Texanol	x		x			
13463-73-7	Titanium dioxide	x	*		x		
108-88-3	Toluene		x	x			
121-44-8	Triethylamine		x	x			

Appendix B. Wall Paint chemicals by paint type and function

Casno	Chemical Name	PAINT TYPE		FUNCTION OF CHEMICAL			
		L a t e x	A l k y d	Solvent /Inter- mediate	Pigment	Resin/ Inter- mediate	Additive
95-63-6	Trimethylbenzene(1,2,4)	*	x	x			
526-73-8	Trimethylbenzene(1,2,3)	*	x	x			
108-67-8	Trimethylbenzene(1,3,5)	*	x	x			
1120-21-4	n-Undecane		x	x			
108-5-4	Vinyl acetate	x				x	
88-12-0	Vinylpyrrolidinone	x					x
11138-66-2	Xanthan gum	x				x	
95-47-6	Xylene(o)	*	x	x			
108-38-3	Xylene(mixed)	*	x	x			

Notes:

* indicates a very small quantity of that chemical used in one paint type relative to the other.

**** - Iron oxide has four possible CAS no's: 1345-25-1/ 1332-37-2/ 1317-61-9/ 1309-37-1

- Aluminum silicate has four possible CAS nos:
22707-90-3/14504-95-1/12068-56-3/12141-40-7

HAPs present in wall paints but not detected in the tests include Acrylonitrile, Ethyl acrylate, Ethyl benzene, Methanol, Methyl ethyl ketone, Methyl isobutyl ketone, Styrene, Toluene and Vinyl acetate.

Appendix C. SIS/L Printout for Wall Paint Chemicals

X-LIST INTERSECT OF USER LIST WITH SIS/L LISTS
 ENVIRONMENTAL PROTECTION AGENCY
 OFFICE OF POLLUTION PREVENTION & TOXICS
 SCREENING INFORMATION SYSTEM/LAN

CAS NO.	Inv	USHV	CORR	8(e)	FYI	HEAST	IRIS	RM(x)	MTL	SIDS	RoL	313	302	110	SDWA
WQCD DWHA	AIR	FIFRA	OSHA	NIOSH	ACGIH										
50-00-0	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
X	X	X	X	X	X										
57-55-6	X	X	X	X	X	X	X	X	X	X	X				
	X	X		X											
62-38-4	X			X	X	X	X				X		X	X	
				X	X										
67-56-1	X	X	X	X	X		X	X	X	X	X	X		X	
X	X	X	X	X	X										
67-68-5	X	X	X	X	X			X			X				
				X											
71-55-6	X	X	X	X	X	X	X	X	X		X	X		X	X
X	X	X	X	X	X										
75-07-0	X		X	X	X		X				X	X			
	X		X	X	X										
75-65-0	X	X	X	X	X			X			X	X			
				X	X										
78-93-3	X	X	X	X	X	X	X	X	X	X	X	X		X	
	X		X	X	X										
80-62-6	X		X	X	X	X	X	X			X	X		X	
	X		X	X	X										
84-74-2	X	X	X	X	X	X	X	X			X	X		X	
X	X														
85-44-9	X	X	X	X	X	X	X	X			X	X			
	X		X	X	X										
88-12-0	X			X											

CAS NO.	Inv	USHV	CORR	8(e)	FYI	HEAST	IRIS	RM(x)	MTL	SIDS	RoL	313	302	110
SDWA	WQCD	DWHA	AIR	FIFRA	OSHA/NIOSH/ACGIH									
12141-46-7	X													
13463-67-7	X			X	X			X				X		
13586-82-8	X			X	X			X						
13845-36-8	X				X									
14504-95-1	X				X									
14807-96-6	X				X			X						
22708-90-3	X				X									
24806-32-4	X													
25265-77-4	X			X				X	X	X	X			
26761-40-0	X				X			X			X			
54193-36-1	X				X									
61203-99-4	X													
61789-51-3	X				X			X			X			
68910-52-1	X				X									
9	12	12	22	28	45	61	47	51	14	11	56	32	6	24
				6	29	80	38							

✓ = Invalid CAS Number

Inv = TSCA Inventory
 CUS = Chemical Update System
 USHV = United States High Vol.
 CORR = CORR
 8(d) = TSCA 8(d) System

SECT4	=	TSCA Section 4 Study	
8 (e)	=	Section 8(e) Notice	
FYI	=	FYI Submission	
CHIP	=	Chem. Hazard Info. Profile	
SUB	=	Substitute Hazard Profile	
HEAST	=	HEAST	
CURE	=	Chemical Unit Record Estimate	
IRIS	=	Integrated Risk Info. System	
UCSS	=	Used Cluster Scoring System	
PEPS	=	Production/Exposure Profiles	
RM(x)	=	OPPT's Existing Chem Program	
MTL	=	Master Testing List	
SIDS	=	Screening Info. Data Set	
RoL	=	Register of Lists	
313	=	EPCRA Section 313	
302	=	EPCRA Section 302	
110	=	SARA Section 110	
			DWHA = Drinking Water Health Advisory
			SDWA = Safe Drinking Water Act
			WQCD = Water Quality Criteria Docs
			FIFRA = Active Ingredients
			NIOSH = NIOSH Chemicals
			OSHA = OSHA Chemicals
			INERT = Inert Ingredients
			ACGIH = ACGIH Chemicals
			AIR = Office of Air Toxics

Appendix D. Human Health Hazard Ranking Criteria from the Use Cluster Scoring System

DATA ELEMENT	DATA QUALITY	RANKING		
		HIGH (3)	MEDIUM(2)	LOW (1)
CARCINOGENS				
If WOE = A or B then				
q1' (Cancer Potency)	High	>1/mg/kg/day	0.01 - 1 /mg/kg/day	<0.01/mg/kg/day
RQ Potency Factors	High	>10/mg/kg/day	0.2 - 10 /mg/kg/day	<0.2/mg/kg/day
Structure Activity Team Rank	Low	High	Medium, med-high	Low, low-medium
Chemical Category Human toxicity Estimate	Low	3	2	1
TSCA Sec. 8(e) Submission	Low/Consistency	3	2	1
If WOE = C then				
q1' (Cancer Potency)	High	>10/mg/kg/day	0.1 - 10 /mg/kg/day	<0.1/mg/kg/day
RQ Potency Factors	High	>80/mg/kg/day High	1 - 80 /mg/kg/day	<1/mg/kg/day
Structure Activity Team Rank	Low	3	Medium, med-high	Low, low-medium
Chemical Category Human Toxicity Estimate	Low	3	2	1
TSCA Sec. 8(e) Submission	Low/Consistency		2	1

If WOE = Unclassified then				
Structure Activity Team Rank	Low	High	Medium, med-high	Low, low-medium
Chemical Category Human Toxicity Estimate	Low	3	2	1
TSCA Sec. 8(e) Submission	Low/Consistency	3	2	1
NONCARCINOGENS				
Reference Dose (RfD)	High	<0.001 mg/kg/day	0.001-0.1 mg/kg/day	>0.1 mg/kg/day
Reference Concentration (RfC)	High	<0.002 mg/m ³	0.002 - 0.2 mg/m ³	>0.2 mg/m ³
Reportable Quantity (RQ)	High	1, 10 lb	100, 1,000 lb	5,000 lb 1000,
Threshold Planning Quantity (TPQ)	High	1, 10 lb	100, 500 lb	10,000 lb
Human Health Water Quality Criteria (HWQC)	High	<1 mg/l	1 - 10 mg/l	>10 mg/l
Chronic NOAEL	Medium	<0.1 mg/kg/day	0.1 - 10 mg/kg/day	>10 mg/kg/day
Chronic LOAEL	Medium	<1 mg/kg/day	1 - 100 mg/kg/day	>100 mg/kg/day
Subchronic NOAEL	Medium	<1 mg/kg/day	1 - 100 mg/kg/day	>100 mg/kg/day
Subchronic LOAEL	Medium	<10 mg/kg/day	10 - 1000 mg/kg/day	>1000 mg/kg/day
Human Health Structure Activity Team Rank	Low	High	Medium, med-high	Low, low-medium
Chemical Category Human Toxicity Estimate	Low	3	2	1
TSCA Sec.8(e) Submission	Low/Consistency	3	2	1

Source: EPA. 1993. Chemical Use Clusters Scoring Methodology.

Appendix E : Summary Statistics for Air Concentrations of Acetaldehyde and Formaldehyde Concentrations Measured in Air from the ITC Study

ACETALDEHYDE						
Sampling Phase	Application Method	Air Changes/ Hour	n/N (c)	Geometric Average (ppm)	Range of Detectable Concentrations (ppm)	Average Environmental Limit of Detection (ppm)
During Application (a)	Airless Spray	0.5	3/3	15.39	12.48 - 19.29	0.52
		5.0	3/3	10.47	9.10 - 11.68	0.53
	Roll	0.5	3/3	12.59	12.21 - 13.10	0.38
		5.0	3/3	5.21	4.31 - 6.34	0.36
During Application and Drying (b)	Airless Spray	0.5	6/6	4.41	2.87 - 6.73	0.03
		5.0	6/6	0.95	0.69 - 1.09	0.03
	Roll	0.5	6/6	4.20	3.63 - 5.41	0.03
		5.0	6/6	0.63	0.57 - 0.67	0.03

FORMALDEHYDE						
Sampling Phase	Application Method	Air Changes/ Hour	n/N (c)	Geometric Average	Range of Detectable Concentrations (ppm)	Average Environmental Limit of Detection (ppm)
During Application (a)	Airless Spray	0.5	3/3	0.44	0.36 - 0.54	0.19
		5.0	3/3	0.30	0.28 - 0.34	0.19
	Roll	0.5	3/3	0.34	0.27 - 0.43	0.14
		5.0	3/3	0.25	0.22 - 0.29	0.13
During Application and Drying (b)	Airless Spray	0.5	6/6	0.28	0.24 - 0.38	0.01
		5.0	6/6	0.05	0.04 - 0.06	0.01
	Roll	0.5	6/6	0.24	0.20 - 0.38	0.01
		5.0	6/6	0.05	0.04 - 0.07	0.01

A = Personal Breathing Zone Samples

B = 6-hour TWA

C = Number of samples with concentrations above the analytical limit of detection/Total number of samples

Appendix F: Source Term Model for DGBE

A model has been developed for estimating emission profiles for chemicals released from interior latex paints, where data are available from small-chamber experiments (Geomet 1997).

The emission profile is based on chamber data from "Methodology for Characterizing Indoor Air Emissions from Latex Paint", test 7 (EPA 1995). In this study, SW 99 and RTI latex paints were applied to pre-painted gypsum board, and chemical concentrations in air were measured. These chamber results were used to develop emission parameters and rate constants for the source term equation below. The SW 99 chamber test results were selected for this assessment. These results are similar to the RTI paint concentrations, except that the peak concentrations are higher by about a factor of 3 for the SW 99 paint (EPA 1995).

The source term was represented by a double exponential. The first exponential represents the "fast" emission rate that occurs primarily when the paint is in the wet phase of the drying process. The second exponential represents the "slow" emission rate that occurs during the dry phase. The following equation shows the time-varying source strength for a double exponential during a continuous painting event (Geomet 1997):

$$S(t) = \frac{M}{t_a} [f(1 - e^{-k_1 t}) + (1-f)(1 - e^{-k_2 t})] - \frac{M}{t_a} [f(1 - e^{-k_1(t-t_a)}) + (1-f)(1 - e^{-k_2(t-t_a)})] H(t-t_a)$$

where

$S(t)$ = Source strength (mg/hr)
 M = Total mass to be emitted (mg)
 t_a = Paint application time (hours)
 f = Fraction of mass emitted from the first exponential
 k_1 = First-order rate constant for first exponential (1/hours)
 k_2 = First-order rate constant for second exponential (1/hours)
 t = Time (hours)

and $H(t-t_a)$ = 0 if $(t-t_a) < 0$
= 1 if $(t-t_a) > 0$

In addition, an attribute specific to the modeled painting event needs to be defined:

M_{EV} = Mass of paint applied during exposure event (mg)

Several of the parameters to this equation must be estimated from the available chamber data. The following user inputs are required (Geomet 1997):

User Inputs

1. Concentration vs. time profiles from chamber tests for DGBE in latex paint with a gypsum board substrate.
2. M_{CH} = Mass of paint applied during chamber test (mg)
3. M_{EV} = Mass of paint applied during exposure event (mg)
4. T_a = Duration of event (hours)

Step 1: Fit Double Exponential to Chamber Data

a. Use nonlinear regression to estimate the parameters of the single exponential that best fits the data after 48 hours. This exponential represents the second exponential in the double exponential (the "slow" emission). The equation representing the concentration in the chamber with a constant air flow and a single exponential source is:

$$C(t) = \frac{E_{02}}{V(\frac{Q}{V} - k_2)} (e^{-k_2 t} - e^{-\frac{Q}{V} t})$$

where

- C = Concentration in the chamber (mass/volume)
- V = Volume of the chamber
- Q = Air flow rate into and out of the chamber (volume/time)
- E_{02} = Initial emission rate for the second exponential (mass/time)
- k_2 = First-order rate constant for the second exponential (time⁻¹)
- t = Time (t > 48 hours)

Each of the parameters is known from the chamber test conditions except E_{02} and k_2 , which are estimated with nonlinear regression analysis (Geomet 1997).

b. Use nonlinear regression to estimate the parameters for another single exponential, such that this exponential fits the difference between the data and the predicted concentrations from the exponential that best fits the data after 48 hours. The equation representing the concentration in the chamber with a constant air flow and the double exponential source is:

$$C(t) = \frac{E_{01}}{V(\frac{Q}{V} - k_1)} (e^{-k_1 t} - e^{-\frac{Q}{V} t}) + \frac{E_{02}}{V(\frac{Q}{V} - k_2)} (e^{-k_2 t} - e^{-\frac{Q}{V} t})$$

where

E_{01} = Initial emission rate for first exponential (mass/time)
 k_1 = First-order rate constant for first exponential (1/time)

Operationally, this can be accomplished by using all the data and inputting the fitted parameters E_{02} and k_2 from step a as "knowns," leaving only two parameters to be estimated, E_{01} and k_1 (Geomet 1997).

Step 2: Estimate Parameters to Equation 1

$$M = \left[\frac{E_{01}}{k_1} + \frac{E_{02}}{k_2} \right] \frac{M_{EV}}{M_{CH}}$$

$$f = \frac{E_{01}}{k_1 * \left(\frac{E_{01}}{k_1} + \frac{E_{02}}{K_2} \right)}$$

where

k_1 = fitted parameter from step 1b
 k_2 = fitted parameter from step 1a

Step 3: Calculate emission profile

Using the parameters calculated above, implement Equation 1 to give the emission rate as a function of time (Geomet 1997). Modeling parameters used in this assessment are shown in the following table.

Table F-1: Modeling Parameters for DGBE Source Term Calculation

Variable	Value (units)	Source
Source of Chamber data	---	"Methodology for Characterizing Indoor Air Emissions from Latex Paint", test 7 (EPA 1995)
Emission parameter, first exponential (E01)	0.2530 mg/hr	Regression of test 7 chamber data from EPA 1995 (Geomet 1997)
Rate constant, first exponential (k1)	0.1584 1/hr	Regression of test 7 chamber data from EPA 1995 (Geomet 1997)
Emission parameter, second exponential (E02)	0.02246 mg/hr	Regression of test 7 chamber data from EPA 1995 (Geomet 1997)
Rate constant, second exponential (k2)	0.009896 1/hr	Regression of test 7 chamber data from EPA 1995 (Geomet 1997)
f and (1-f) (Fractions for 1st and 2nd exponentials)	f is .4, 1-f is 0.6	Geomet 1997
Mass of paint applied during chamber test (Mch)	3820 mg	"Methodology for Characterizing Indoor Air Emissions from Latex Paint", summary of parameters for test 7 (EPA 1995)
Mass of paint applied during exposure event	19,200,000 mg	Calculated from the estimated surface area painted during the work day (Geomet 1997)
Total mass to be emitted (M)	18,980 mg	Calculated from the previous parameters (Geomet 1997)
Time of application, Ta	8 hours	
M/Ta	2429 mg/hr	
Weight fraction of DGBE in SW 99	4.98 mg/g	EPA 1995

Appendix G: Estimating DGBE Concentrations and Exposures

The Multi-Chamber Concentration and Exposure Model (MCCEM) was used to generate the DGBE concentration in air from the source term described above. MCCEM is a user-friendly computer program that estimates indoor concentrations for, and inhalation exposure to, chemicals released from products or materials in residences.

Table G-1. Default Values for DBGE Exposure Scenario

Input Variable	Value	Notes
House Volume	369 m ³	Personal communication with Mike Koontz based on his analysis of the PFT Database and the Department of Energy's "Residential Energy Consumption Survey" (Koontz 1996)
Zone 1	161 m ³	The zone volume was determined from the estimated surface area painted
Square Feet Painted	1536 ft ²	Surface area painted was determined from the amount of time spent painting and the application rate. Amount painted was four walls and ceiling. 1 m ³ = 35.3 ft ³ .
Square Feet in Zone	1562.5 ft ²	Includes one window (2'x 3.25') and one door (3'x 6.67'). Window and door are not painted
Dimensions of zone	height 8', length and width 26.65'	Length and width derived from estimated surface area in zone.
Amount of Paint used	3.84 gallons, 19200 grams*	One gallon of paint is assumed to cover 400 square feet (one coat)
Infiltration Rate	0.45 ACH	From the PFT Database; average (Fall) value (Koontz 1996)
Hours worked per day	8	Standard Agency assumption for workers
Days worked per year	141	250 days/year painted x 90% spent using latex paint x 63% of time spent indoors (Hackney 1996)
Years worked per lifetime	40	Standard Agency assumption for workers
AT (days)	10950	Number of days in a working lifetime (30 years x 365 days)

*conversion: 1 gallon = 5000 grams (Kodak report) 1 gallon = 128 ounces, therefore, 1 ounce = 39 grams

Determination of Surface Area Painted and Room Volume for DGBE Exposure Calculations

Surface Area Painted was determined by multiplying the application rate of 3.2 square feet per minute with the exposure duration. This yielded an estimated surface area painted (measured in square feet).

The volume of the zone of use was calculated from the estimated $x^2 + 32x$ = estimated surface area covered; where x is the length and width of the walls in the room and x^2 represents the surface area of the ceiling, and $32x$ represents the surface area of the walls. In other words, to estimate the ceiling's surface area, one multiplies the length and width of the walls. To estimate the surface area of one of the walls, one multiplies x (the length or width) with 8, the height. This number is then multiplied by 4 to obtain the surface area for all four walls. Once the length, width, and height are obtained, they are multiplied to get the room volume in cubic feet. This number is then divided by 35.3 to obtain the volume in meters cubed.

Determination of Air Exchange Rates:

The air exchange rates were determined by multiplying the infiltration rate and the appropriate volume. The infiltration rate selected was 0.45. The air exchange rates are shown in the following table.

Table G-2: Air Exchange Rates

Zone 1 volume	Zone 2 volume	Air Flow (m ³ /hr)		
		Zone 0-1	Zone 0-2	Zone 1-2
161 m ³	208 m ³	72.5	93.6	80.3

Note: all air exchange rates are assumed to be equal in both directions; i.e., zone 0-1 is the same as zone 1-0.

The equations for determining air exchange rates are as follows (Koontz 1996):

Zone 0-1 and zone 0-2 (and vice versa):
 air flow (m³/hr) = Infiltration rate x zone volume

Zone 1-2:
 air flow (m³/hr) = (0.078 + 0.31*a) * V

where: a = infiltration rate
 V = house volume



EPIDEMIOLOGY RESOURCES INC.

The New England Epidemiology Institute

November 11, 1998

Clay B. Frederick Ph.D.
Senior Research Fellow in the Toxicology Department
Rohm and Haas Co.
727 Norristown Road
Spring House PA 19477-0904

Dear Dr. Frederick:

You have asked me to comment on my study¹ of colon and rectal cancer in ethyl acrylate (EA) and methyl methacrylate (MMA) workers, in light of the Basic Acrylic Manufacturers, Inc. (BAMM) Petition to Delist Ethyl Acrylate from the Biennial Report on Carcinogens. To that end, I have reviewed the petition and most of the supporting documentation, I have examined the draft background document for ethyl acrylate prepared by the NTP staff for the December 2-3 meeting of the NTP Board of Scientific Counselors, and I have refamiliarized myself with my own study.

The essence of our work was this. We reviewed mortality in two wartime cohorts of workers who were exposed to both EA and MMA in the manufacture of Plexiglas, and one later cohort of workers who were exposed essentially only to MMA. In our paper and the commentary, these have been referred to as the Early Bristol, Knoxville, and Later Bristol cohorts respectively. We used personnel records to identify the jobs to which the workers were assigned. On the basis of recollections of workers who could be contacted in the 1980s and exposure measures taken in the 1970s, Lester DeFonso of Rohm and Haas, one of our coauthors, created ordered, but largely qualitative exposure scales that ranged from no exposure to "high" exposure. High exposure resulted from an exothermic mixing step carried out in open containers in a closed shed during the wartime production years. This was known as the "boil out" process, and was discontinued as I understand it not long after the end of the Second World War. We examined three different threshold levels of cumulative vapor exposure and three different time periods following each threshold in a systematic search for combinations of exposure and induction periods that might be related to colorectal cancer. For each exposure-threshold combination, we employed both additive and multiplicative rate models to search for an effect. We also examined maximal exposure in two different time periods. We found an elevation of colon cancer of 11 observed cases versus 4.58 expected among Early Bristol workers in the highest exposure category at the longest induction period (20 years). There were 3 cancers of the rectum, as opposed to 1.06 expected in the same subgroup of the Early Bristol cohort. In the high exposure, long-induction portion of the later Bristol cohort experience there were no cases of cancer of the colon or

¹Walker Am, Cohen AJ, Loughlin JE, Rothman KJ, DeFonso L. Mortality from cancer of the colon or rectum among workers exposed to ethyl acrylate and methyl methacrylate. *Scan J Work Environ Health* 1991;17:7-19

Clay Frederick
November 11, 1998
Page 2

rectum, with 0.27 expected, and in the corresponding part of the Knoxville experience there was 1 case, with 1.95 expected.

The evidence in favor of a causal relationship stems from finding the excess risk for the Early Bristol cohort in the dose and induction period stratum where one would have postulated a priori a maximum observable effect. While there are many serious limitations to inference from this study, there is no specific hypothesis, other than chance, that would lead to seeing the small excess that we did observe in the high-dose, long-induction-period part of the cohort.

In the original publication we cited a number of reasons why our data should not be taken on their own as proof of a causal association, and these have been largely summarized, correctly, in the NTP staff document. An increase on the order of two to three fold in risk should have been detectable in the Knoxville cohort, and it was not seen. The exposure indices were crude for all the cohorts. We could not distinguish between EA and MMA in the one cohort that showed an effect (Early Bristol). There were other carcinogens in the workplace. There is (and we can say this more strongly today than seven years ago) no plausible, known causal mechanism for an effect on the colon and rectum resulting from vapor exposures to EA and MMA.

There was another serious limitation, which we cited in the introduction to our report, that has not been adequately highlighted by either BAMM or the NTP draft. We undertook the analysis because we knew in advance that there was an excess of colon cancer in the cohort. These cohorts had been assembled originally for the evaluation of lung cancer risk, and completely after the fact DeFonso and his colleagues noted a small excess of colon cancer. From that point, we undertook to rigorously structure an analysis that would pinpoint and quantify the elevation. But it remains a post hoc analysis of an unexpected finding. If there were other, supportive human data, I would not think of this as a special drawback. But standing alone, the report is less persuasive than it would have been if colorectal cancers had been identified independently as a concern for these workers.

For all of these reasons, I find that I agree with the NTP staff that "This study, by itself, can neither establish nor rule out a causal relationship with cancer."

Sincerely,

A handwritten signature in dark ink, appearing to read "Alexander M. Walker", with a stylized, cursive script.

Alexander M. Walker



TOXICOLOGICAL REVIEW

of

METHYL METHACRYLATE

(CAS No. 80-62-6)

**In Support of Summary Information on the
Integrated Risk Information System (IRIS)**

January 1998

U.S. Environmental Protection Agency
Washington, DC

implants, Ferguson (1977) suggests that sarcomas that arise following subcutaneous implants of poly-MMA can be attributed to mechanical processes involving topographic interaction of the solid surface with normal cells, especially macrophages. Consistent with this explanation are the experiments of Oppenheimer et al. (1955), in which no tumors were induced when monomeric MMA was applied dermally to the back of the neck of rats. However, the exposure period in the Oppenheimer study was just 4 mo and only 10 animals were tested.

In the studies by Hazelton Laboratories (1979a,b), Fischer 344 rats and Charles River Lakeview Golden Hamsters were exposed to MMA vapors at 0, 25, 100, and 400 ppm for 6 h/day for 5 days/week for 2 years and 18 mo, respectively. No increase was seen in the number or type of tumors in either rats or hamsters, indicating that MMA was not carcinogenic in these two species under those conditions. Appearance of a polypoid adenoma in the nasal cavity of two MMA-exposed male rats (one each from the 100 and 400 ppm groups) (Lomax, 1992; Lomax et al., 1997) is not likely to be associated with MMA-exposure as these benign neoplasms have been reported in control rats as well (Miller et al., 1985). Similarly, a 2-year NTP inhalation bioassay of rats and mice exposed to up to 1,000 ppm gave negative results for carcinogenicity, although the animals may not have been tested at the maximum tolerated dose (NTP, 1986; Chan et al., 1988).

Borzelleca et al. (1964) reported the absence of carcinogenic effects in groups of 25 male and 25 female Wistar rats given drinking water containing 0, 6, 60, or 2,000 ppm MMA for 2 years. Taken together, the genotoxicity, chronic inhalation, and chronic oral studies available suggest that MMA is not carcinogenic in laboratory animals.

4.6.2. Human Evidence

Limited epidemiological data are available to determine whether the incidence of various malignancies is higher in groups occupationally exposed to MMA versus those not exposed, and no studies have been reported on whether smoking is a related factor in the occurrence of malignancies in MMA-exposed workers. One retrospective epidemiological study that relates to malignancies was conducted at the Bristol Plant, PA, which manufactures plastics, leather chemicals, etc. (Monroe, 1984; Walker et al., 1991). In this study of Bristol Plant employees hired prior to 1946 (Early Bristol cohort), an excess of cancer of the large intestine and rectum was noted. However, an increase in these types of cancers was not observed in similar populations at separate sites, or in subsequent evaluations of the same site (Walker et al., 1991; ECETOC, 1995; Collins et al., 1989). Collins et al. (1989) have noted that during the 1970s, the county in which the plant was located had a high colorectal cancer rate, at the 75th percentile for the United States.

Some evidence of an increased death rate from cancer and noncancer respiratory disease is provided by the American Cyanamid (Collins et al., 1989) and Knoxville (Walker et al., 1991) cohorts. However, in both of these cohorts, exposure to MMA was considerably lower than in the Early Bristol cohort, which showed no such excess. Others have suggested that these increases were lifestyle related (ECETOC, 1995).

4.6.3. Structure-Activity Relationships

Acrylic acid, four monofunctional acrylates, eight polyfunctional (di- or tri-) acrylates, a dimethacrylate, and a trimethacrylate have been tested in skin painting cancer bioassays. Acrylic acid, 2-ethylhexyl acrylate, and three diacrylates caused skin tumors. Methyl acrylate (MA), ethyl acrylate (EA), n-butyl acrylate (BA), and methyl methacrylate have been tested in chronic inhalation bioassays and found to be negative with respect to carcinogenicity (Woo et al., 1988). While the Borzelleca et al. (1964) drinking water studies did not report carcinogenicity for either EA or MMA exposure, EA was found to cause forestomach tumors following gavage exposure (NTP, 1983). However, the fact the EA has been found to cause forestomach tumors at high gavage doses (NTP, 1983) does not necessarily implicate MMA. This is suggested by structure-activity relationship studies that demonstrate that the addition of a methyl group to the acrylate moiety tends to abolish carcinogenic activity (Woo et al., 1988) and gavage dosing of analogues of EA demonstrating that the forestomach toxicity required the intact molecule (an ester moiety, the double bond, and no substitution at carbon number 2) (Ghanayem et al., 1985). In another paper, Ghanayem et al. (1986) reported that cell proliferation of the rat forestomach (believed to be a precursor effect to tumors caused by this compound) was apparent in all rats (12/12) following 2-week gavage administration of EA at both 100 and 200 mg/kg, but was not apparent in any rats exposed to 100 mg/kg MMA (0/8) and in just 1/8 rats exposed to 200 mg/kg MMA. This latter increase was not statistically significant and the effect was much less severe than the effects caused by EA at either dose. Thus, structure-activity relationship analysis does not suggest that MMA would be carcinogenic by any route.

4.6.4. Summary

Cases of sarcomas reported following implants of polyMMA are attributed to mechanical processes, not MMA. Carcinogenic activity was not detected in four well-conducted chronic inhalation bioassays in three different species: rats, mice, and hamsters (NTP, 1986; Hazelton, 1979a,b). Results of a 2-year drinking water study of Wistar rats (25/sex) (Borzelleca et al., 1964), though not as well documented as the inhalation studies, also showed no carcinogenicity. Mutagenicity data are mixed and human epidemiologic evidence is inadequate for basing a carcinogenicity determination. Under the Proposed Guidelines for Carcinogenic Risk Assessment (U.S. EPA, 1996a), MMA is considered *not likely to be carcinogenic to humans* because it has been evaluated in two well-conducted studies in two appropriate animal species without demonstrating carcinogenic effects.

4.7. Other Hazard Identification Issues

4.7.1. Possible Childhood Susceptibility

A number of factors may differentially affect children's responses to toxicants. The only toxicity information on MMA of possible relevance to this issue is that several studies showed that developmental effects are observed only at exposure levels that are maternally toxic, even lethal. There is too little information to make any further statements about how children may be differentially affected by methyl methacrylate, as there are no data regarding methyl methacrylate

The following journal articles were attached to the comments of the Basic Acrylic Monomer Manufacturers, Inc. (BAMM). Due to copyright infringement laws we cannot display them. We listed the citations for your information.

National Toxicology Program
Report on Carcinogens Group

Ciaccio PJ, Gicquel E, O'Neill PJ, Scribner HE, Vandenberghe YL. 1998. Investigation of the positive response of ethyl acrylate in the mouse lymphoma genotoxicity assay. *Toxicol Sci* 46: 324-332.

Hilliard CA, Armstrong, MJ, Bradt CI, Hill, RB, Greenwood SK, Galloway SM. 1998. *Environ Mol Mutagen* 31:316-326.

Nylander-French LA, French JE. 1998. Tripropylene glycol diacrylate but not ethyl acrylate induces skin tumors in a twenty-week short-term tumorigenesis study in Tg.AC (v-**Ha**-*ras*) mice. *Toxicol Pathol* 26(4):476-483.